DOCUMENT RESUME

ED 149 972 SE 023 413

AUTHOR Westerhold, Arnold F., Ed.; Bennett, Ernest C., Ed.
TITLE A Manual of Simplified Laboratory Methods for Operators of Wastewater Treatment Facilities.
INSTITUTION Illinois State Environmental Protection Agency, Springfield.
PUB DATE Apr 74
NOTE 94p.; Pages 1-1 through 1-12 (General Introduction) removed due to copyright restrictions; Section 8 missing; Contains occasional light type; Best Copy Available

EDRS PRICE MF-$0.83 HC-$4.67 Plus Postage.
DESCRIPTORS Chemistry; Environmental Education; *Environmental Technicians; Independent Study; *Instructional Materials; Job Skills; *Laboratory Techniques; *Pollution; *Post Secondary Education; Public Health; *Water Pollution Control
IDENTIFIERS *Waste Water Treatment

ABSTRACT

This manual is designed to provide the small wastewater treatment plant operator, as well as the new or inexperienced operator, with simplified methods for laboratory analysis of water and wastewater. It is emphasized that this manual is not a replacement for standard methods but a guide for plants with insufficient equipment to perform analyses in accordance with standard methods. Each of the sections is designed to be complete within itself. The tests and measurements presented include: acids, biochemical oxygen demand (BOD), dissolved oxygen, residues, sludge, and suspended solids. (CS)

****
* Reproductions supplied by EDRS are the best that can be made *
* from the original document. *
****

ED149972

U S DEPARTMENT OF HEALTH
EDUCATION & WELFARE
NATIONAL INSTITUTE OF
EDUCATION

THIS DOCUMENT HAS BEEN REPRODUCED EXACTLY AS RECEIVED FROM THE PERSON OR ORGANIZATION ORIGINATING IT. POINTS OF VIEW OR OPINIONS STATED DO NOT NECESSARILY REPRESENT OFFICIAL NATIONAL INSTITUTE OF EDUCATION POSITION OR POLICY

A MANUAL OF SIMPLIFIED LABORATORY METHODS FOR OPERATORS OF WASTEWATER TREATMENT FACILITIES

Compiled by the Illinois Environmental Protection Agency

"PERMISSION TO REPRODUCE THIS MATERIAL HAS BEEN GRANTED BY

E. Bennett
Ill. EPA

TO THE EDUCATIONAL RESOURCES INFORMATION CENTER (ERIC) AND USERS OF THE ERIC SYSTEM."

Editors: Arnold F. Westerhold
Co-ordinator of Chemistry
Division of Laboratory Services

Ernest C. Bennett, P.E., Manager
Operator Certification & Training Unit
Division of Water Pollution Control

SE 023 413

A MANUAL OF SIMPLIFIED LABORATORY METHODS FOR OPERATORS OF WASTEWATER TREATMENT FACILITIES

Compiled by the Illinois Environmental Protection Agency

Editors: Arnold F. Westerhold
Co-ordinator of Chemistry
Division of Laboratory Services

Ernest C. Bennett, P.E., Manager
Operator Certification & Training Unit
Division of Water Pollution Control

* *

DISCLAIMER: Mention of trade names or commercial products does not constitute endorsement by the Illinois Environmental Protection Agency.

100 % Recycled Paper

TABLE OF CONTENTS

PREFACE

	Section
INTRODUCTION TO TESTING	1
1. General introduction	
2. Grades and qualities of chemicals	
3. Form of chemicals	
4. Sampling of sewage	
5. Glass volumetric apparatus care and handling	
6. Laboratory apparatus and supplies	
7. Colorimetry	
LABORATORY TESTS AND MEASUREMENTS	
Acids, organic (colorimetric method)	2
Acids, organic (column chromatographic method)	3
Acids, volatile	4
Activated sludge settleability	19
Alkalinity	5
Biochemical oxygen demand	9, 10
Chlorine, residual	6
Cyanide (colorimetric method)	7
Density index, sludge	21
Dissolved oxygen	11, 12
Loading, Plant	8
Mixed liquor, suspended solids (MLSS)	16
Organic acids	2, 3
Oxygen demand, biochemical (Graduate dilution method)	9

Oxygen, demand, biochemical (Simplified non-standard method)	10
Oxygen, dissolved, effluent	11
Oxygen, dissolved, mixed liquor	12
Oxygen, demand index	13
pH	14
Plant loading	8
Residue, on evaporation	15
Residue, suspended, mixed liquor (MLSS)	16
Residue, suspended, total and volatile	17
Residual, chlorine	6
Return sludge (MLSS)	16
Settleable matter (Imhoff cone technique)	18
Settleability (activated sludge)	19
Sludge, age	20
Sludge, density index	21
Sludge, solids, total and volatile (Anaerobic digesters)	22
Sludge, volume index	23
Solids (see: Residue)	
Suspended solids (total and volatile)	17
Temperature	24
Volatile acids (also see: Acids, organic)	4

Some tests occasionally used by treatment plant operators are complex and beyond the capability of most operators or waste treatment plants and are not included here. For these procedures follow the detailed procedures contained in the current edition of "Standard Methods for the Examination of Water and Wastewater", or consult with your nearest consulting laboratory or consulting engineering firm.

PREFACE

Standard Methods for the analyses of water and wastewater has long been established as the accepted authority on laboratory methods for use in water and wastewater treatment facilities' laboratories. Where laboratories are adequately equipped, and technicians properly trained, it should continue to be the guide for all laboratory analyses.

However, in many small plants, laboratories are insufficiently equipped to perform analyses in accordance with Standard Methods. In other cases, new or inexperienced operators lack the technical knowledge and training necessary to properly utilize Standard Methods. In these instances, simple but adequate analytical methods are required in order to provide the operator with information necessary to intelligent process control decisions. This manual then is an attempt to provide the small plant - as well as the new or inexperienced operator, with simplified methods - for laboratory analysis of water and wastewater. Although not necessarily as accurate as the methods outlined in Standard Methods, the results of these analyses will generally be adequate for their intended purpose. In a number of cases, it is not felt that there is a practical, simplified method and so the laboratory technician is referred to Standard Methods for the appropriate methods of analysis. In all cases where a simplified laboratory method is not provided or where the operator believes his equipment and personal technical mastery sufficient, Standard Methods should be employed.

This manual would be incomplete if appropriate credit were not given to those whose extra efforts have made it possible. Credit must be given to the Division of Laboratory Services, and in particular to Mr. Arnold Westerhold who has served as an editor of this manual and to his able assistant Dr. David Schaeffer. Mr. Westerhold and Dr. Schaeffer have assembled, edited, tested, and in a number of instances developed the simplified methods presented.

Their technical and professional expertise have been relied upon heavily in determining the contents of this manual.

Credit must also be given to the American Water Works Association publishers of AWWA Manual M12 and to Dr. Kenneth D. Kerri, Sacramento State College, Sacramento California, under whose direction the Environmental Protection Agency manual Operation of Wastewater Treatment Plants was prepared, for their kindly permitting us to reproduce parts of their respective publications. Wherever such reproduction has occurred, we believe appropriate credit has been noted.

The design, printing, and distribution of the manual has been under the direction of the Operator Certification and Training Unit of the Division of Water Pollution Control, Ernest Bernett, P.E., Manager of the Operator Certification and Training Unit, has served as an editor of the manual. As with any work of this nature, some errors are

likely to slip past the closest proofreading scrutiny. We apologize for any inconvenience such errors may cause and trust that our readers will bring them to our attention so they may be corrected in subsequent editions. This manual has been formatted in what is some times termed an "evergreen" document. Each section is designed to be complete in itself with the manual as a whole being designed so that individual sections may be added, deleted, or updated without destroying the usefulness of the entire manual. As new sections are developed, and old section revised, it will be possible for the individual operator and laboratory technician to add to or correct his existing manual so that it is always "evergreen". We trust that the intended user will find the three-hole punched sectionalized format both convenient and useful. Your comments and recommendations for future publication will be appreciated. Questions and comments should be addressed to; Manager, Operator Certification and Training Unit, Division of Water Pollution Control, Illinois Environmental Protection Agency, Springfield, Illinois 62706.

Ernest C. Bennett, P.E., Manager
Operator Certification and Training Unit
Division of Water Pollution Control
Illinois Environmental Protection Agency

April, 1974

PAGES 1-1 THROUGH 1-12 (GENERAL INTRODUCTION)
REMOVED PRIOR TO BEING SHIPPED TO EDRS DUE
TO COPYRIGHT RESTRICTIONS

GRADES AND QUALITIES OF CHEMICALS

Chemicals are made in several grades based on quality or purity. These qualities are designated by names which vary somewhat among manufacturers. In general, the quality of chemicals used in testing must be high. It will be necessary for the purchaser to read the quality designations in the catalog being used, since designations vary considerably with manufacturers. Although not complete, the following list will give some idea of the grades of chemicals available:

1. Primary standards - Primary standards are reagents of high accuracy assay and are suitable as references and in the preparation of standard solutions.

2. A.C.S. reagent grade - For some chemicals, the American Chemical Society has established standards. Most manufacturers making chemicals meeting these standards list them as A.C.S. Reagent Grade.

3. Reagent grade - This designation is used by some manufacturers to label chemicals of high quality. Many chemicals of reagent grade carry the manufacturer's analysis on the label.

4. C.P. grade - C.P. originally meant chemically pure. This is an older term still in use by some manufacturers to designate the quality of certain chemicals. Generally C.P. quality is good quality but not equal to reagent grade.

5. U.S.P. grade - U.S.P. grade chemicals meet the specifications of the United States Pharmacopeia, a publication establishing standards for chemicals and drugs used as pharmaceuticals.

6. N.F. grade - N.F. grade chemicals conform to the specifications of the National Formulary, a publication establishing standards for chemicals and drugs used in the pharmaceutical trade.

7. Practical grade - Practical grade is a quality designation usually applied to organic chemicals of sufficiently high quality to be suitable for use in many applications.

8. Technical grade - Technical grade chemicals are of commercial quality. Generally technical grade chemicals are not used in the preparation of solutions and reagents for testing purposes. Technical grade sodium dichromate is generally used in the preparation of cleaning solution, however.

9. Other grade - There are other designations of quality such as "Highest Purity", "Purified", or the manufacturer's name grade all of which may be very high quality. It is necessary to read the quality grade designations in the (preface of most) catalogs to determine the qualities listed.

FORM OF CHEMICALS

Frequently, there is a choice available in the form of the chemical to be purchased. In some cases the form used is not critical. In other cases, strict attention must be paid to the form of the chemical to be used and the correct one must be obtained. The following list will explain some of the common forms of chemicals used:

1. Powder - Many chemicals are available in a very fine particle size described as powder.

2. Crystal - Some chemicals are sold in their crystalline form which may be anywhere in size from very fine crystals similar to granulated sugar up to crystals larger than sugar cubes.

3. 4 mesh, 8 mesh, etc. - Some chemicals such as calcium chloride are sized uniformly by screening through sieves such as 4 mesh which is a sieve with 4 wires per inch in each direction.

4. Stick, flake and pellet - Sodium hydroxide may be purchased in the form of sticks which are fairly large, and pellets and flakes which are much smaller in size. In general, pellets of a size somewhat like split peas are most commonly used.

5. Anhydrous - An anhydrous chemical is one without chemically combined water, sometimes called water of crystallization, in the molecule.

6. Hydrated - A hydrated chemical contains water of crystallization in the molecule. Manganous sulfate is available as the monohydrate, dihydrate and tetrahydrate. In all cases it is important that the exact composition of the chemical be noted and the correct weight used when making up solutions.

SAMPLING OF SEWAGE

In order to run tests on sewage, one must have samples. These samples, to be meaningful, must be representative of the material from which it was obtained. The best laboratory analysis is only as good as the sample; however, in many cases the sample collected depends on the information that is to be gained from it.

There are two types of sampling procedures used in sewage plants. These are composite sampling and grab sampling. Composite samples are collected at specified intervals in proportion to flow and mixed to make an average sample representative of the flow. Since sewage is perishable, composite samples should be refrigerated at a temperature less than 10°C during the period of time over which fractions are collected. In general, composite sampling may be done at 1 hr., 2 hr., or 4, hr. intervals over a 24 hr. period. The more frequently the fractions of the composite sample are collected, the more representative the composite sample will be in the total flow.

Sampling points and frequency of collection must be determined for each plant. No schedule of sampling can be devised that would be satisfactory for all plants.

REFERENCES:

Applied Stream Sanitation, Velz, C.J., Wiley Interscience, pp. 401-421.

Methods for the Collection and Analysis of Water Samples for Dissolved Minerals and Gases, Brown, Skougstad, and Fishman, USGS, Chapter A1 Book 5 Laboratory Analysis.

GLASS VOLUMETRIC APPARATUS
CARE AND HANDLING

The following information has been adapted from literature published

By: Kimble Glass Company, Subsidiary of Owens - Illinois

Glass volumetric apparatus comprises a class of objects to measure volume. These volumes are indicated by lines in the outer surface of the glass produced by etching with hydrofluoric acid, or by engraving with a thin metal or abrasive wheel. Since results achieved by etching are superior, this method is used universally to make the best quality apparatus.

In addition to the lines indicating the volumes, the numerical values of these volumes in the particular system of weights and measures used also must be marked on the apparatus. The temperature of calibration also usually appears on the instruments since the volume of a glass vessel changes slightly with temperature.

Finally, the method of use--whether calibrated to contain or to deliver the indicated volume--is marked either as "contains" or as "TC" or "TD".

Some pipets are calibrated to deliver the indicated volume when the small amount remaining in the tip after free delivery has ceased is blown out and added to the main delivery. These pipets sometimes are said to be "Calibrated for blowout". To call attention to this method of calibration an opaque band about 1/8" wide is provided near the top.

STANDARD TEMPERATURE

The standard temperature in the United States for volumetric apparatus is 20°C, and all apparatus is calibrated by manufacturers to contain or deliver the indicated capacity at this temperature, unless a different temperature is specifically requested.

There are several essential rules which must be followed in order to get the best results with volumetric apparatus. These rules concern cleanliness, method of reading the meniscus, and the filling and emptying of the various types of instruments.

CLEANLINESS OF APPARATUS

The usual criterion of cleanliness of glass apparatus is uniform wetting of the surface by distilled water. Certain contaminations,

especially grease, adhering to the walls of the container prevent them from being uniformly wetted, and there is a tendency for water to collect into drops.

Imperfect wetting causes irregularities in capacity of volumetric glassware by distorting the meniscus, and also by affecting the volume of the residue adhering to the walls after the instruments or containers are emptied, since they will not deliver the volume for which they were calibrated. Even when the surface of the vessel is uniformly wetted, variations in the apparent capacity still may occur, due to contamination of the liquid surface by minute quantities of fatty or other organic substances which produce a change in the surface tension affecting the shape of the meniscus. The cleaning, rinsing and drying, therefore, must be carried out in such a way as to prevent this.

The choice of the procedure to be used in cleaning glassware depends on the nature of the contaminant. In many cases special reagents or methods must be used to remove a particular substance. Before listing the more important methods, it is desirable to make a few general statements.

Glasses used in chemical apparatus have excellent resistance to all the common acids. Strong alkaline solutions, such as hot caustic solutions, will attack any glass if contact is prolonged. This is true even though a particular glass may not exhibit any visible effect, due to the solubility of the reaction products. Dilute detergent solutions, up to about 2% strength, will have no serious effect on the glass, unless the glass is exposed for unnecessarily long periods or the detergent is allowed to dry on the glass.

SAFETY PRECAUTIONS: With many pieces of glassware, it is necessary or desirable to fill by suction when cleaning. DO NOT SUCK UP ACID OR OTHER CLEANERS WITH THE MOUTH. Connect the article to an aspirator pump, a vacuum pump, or use a rubber bulb. In the case of a vacuum pump, use a trap in between glassware and pump to prevent fumes or wastes from entering the pump.

ABRASIVES: Do not use abrasives such as "Old Dutch", "Bab-O", etc. on glassware, particularly volumetric ware.

WATER FOR RINSING: When preparing a piece of glassware for use, rinsing with tap water should be followed by a thorough rinsing with distilled water or water which has been put through an ion-exchange device.

ADHERENT ORGANIC RESIDUES: Never attempt to remove such residues by the application of direct heat. Permanent strains may be introduced; and what is more important, the calibration of volumetric apparatus may be changed.

CLEANING METHODS

The cleaning methods given here should cover most of the contaminants.

1. Fill with a sulfuric acid-dichromate mixture and let stand. After removal of mixture, rinse with distilled water at least six times. To make the cleaning mixture, dissolve 60-65 grams of sodium or potassium dichromate by heating in 30-35 ml of water; cool, and slowly add concentrated sulfuric acid to make 1 liter of solution.

2. Scrub with a 1 to 2% warm solution of a detergent such as Calgonite, Dash, All, Tide, etc. Rinse well after brushing. DO NOT HEAT VOLUMETRIC GLASSWARE IN DRYING OVEN.

METHOD OF READING THE MENISCUS

Where water or other wetting liquid is used, the method of reading advised by the National Bureau of Standards is described as follows:

Method of Reading Burets, Pipets, Manometers, etc.

a. Using Water or Other Wetting Liquid -- In all apparatus where the volume is limited by a meniscus, the reading or setting is made on the lowest point of the meniscus. In order that the lowest point may be observed, it is necessary to place a shade of some dark material immediately below the meniscus, which renders the profile of the meniscus dark and clearly visible against a light background. A convenient device for this purpose is a collar-shaped section of thick black rubber tubing, cut open at one side and of such size as to clasp the tube firmly.

   The position of the lowest point of the meniscus with reference to the graduation line is such that it is in the plane of the middle of the graduation line. This position of the meniscus is obtained by making the setting in the center of the ellipse formed by the graduation line on the front and the back of the tube as observed by having the eye slightly below the plane of the graduation line. This is illustrated in figure 1, page 1-20. The setting is accurate if, as the eye is raised and the ellipse narrows, the lowest point of the meniscus remains midway between the front and rear portions of the graduation line. By this method it is possible to observe the approach of the meniscus from either above or below the line to its proper setting.

b. Using Mercury -- In setting a mercury meniscus on a graduation line, the instrument must be tapped sharply in order that the meniscus may assume a normal shape. The highest

FIGURE 1. *Method of setting water meniscus.*

point of the meniscus is set on the middle of the graduation line by employing the principles outlined for water, but observing from above the line.

REFERENCE:

NBS Circular 602, Testing of Glass Volumetric Apparatus.

FILLING AND EMPTYING

The results obtained with volumetric apparatus depend not only on the accuracy with which the ware is calibrated, but also on the method of use.

The following rules have been suggested by the National Bureau of Standards for the most part. These requirements may seem at times to be unduly detailed, but they are based on exact knowledge of the behavior of the various types of apparatus as determined experimentally.

FLASKS: In making up a solution to a definite strength in a volumetric flask, the dilution solution (usually water) should be added to within about 1 inch of the calibration mark. Since the entire neck usually is wet at the time the volume is adjusted, due to the mixing process, a drainage time of about 2 minutes is allowed before filling to the mark.

CYLINDERS: In filling a cylinder the liquid is allowed to flow down one side only.

BURETS: Burets should be clamped in a vertical position and filled to about 1 inch above the "0" line.

The setting to the "0" line is made by opening fully the stopcock, draining the excess liquid into a beaker or other receptical until the liquid is within about 1/4 inch above the "0" mark. This procedure will usually drive out any air trapped in the stopcock or tip. The exact "0" setting is made by opening the stopcock slightly, emptying the liquid drop-by-drop until the bottom of the meniscus is level with the "0" mark. Any liquid remaining at the top after setting has been made is touched-off against the wet side of the receptable.

PIPETS: Pipets also are held in a verticle position and filled to about 20 mm above the "0" line. The technique of setting to this line is the same as used for burets. The rate of outflow at this point is controlled by slight pressure of a finger on the top.

With measuring and serological pipets, delivery is unrestricted, unless the liquid descends so rapidly that it would be impossible to stop at the desired place. In this case, however, delivery should be as fast as possible while retaining control with a finger. The tip is touched to the side of the receiver when delivery is completed and then removed immediately, except for certain types of serological pipets. These are "calibrated for blowout", i.e., to deliver the indicated capacity when the small amount remaining in the tip after free delivery has ceased is blown out and added to the initial volume. As mentioned before, all such pipets are marked with an opaque ring near the top. The use of an initial point other than "0" is not advised for pipets with very rapid delivery.

VOLUMETRIC PIPETS: Are held in a vertical position and outflow is unrestricted until the surface of the water reaches the upper end of the delivery tube. Then the tip is touched to the wet surface of the receiving vessel and kept in contact with it until the water has ceased to flow. The water remaining in the tip is not blown out.

COLORIMETRY

The electromagnetic spectrum consists of many bands such as the radio frequency (radio, t.v.), microwave (ovens), ultraviolet (responsible for suntanning), infrared (heat) or visible regions. Each region consists of a series of distinct points or wavelengths. The distinct points or wavelengths of the visible region are the colors with which we are all familiar: red, orange, yellow, green, blue, indigo, and violet. While these colors can be mixed to give various hues and shades, the original components (i.e., the original colors) can be retrieved in a variety of ways, such as colorimetry.

An important characteristic of color is its intensity. For example, if a drop of ink is added to a glass of water, the intensity of the resulting solution will be low, but the color will still be that of the original ink. These ideas, namely that each color has a characteristic wavelength associated with it and that the intensity of a given color may vary, forms the basis of many analytical methods, including spectrophotometry and colorimetry.

There are at least three simple ways in which the color of an unknown can be compared with the color of a known: (1) visual matching; (2) by use of a color comparator; or (3) use of filters, especially in a colorimeter.

One simple visual matching situation occurs in the titration of an acid with a base. If phenolphthalein is used as an indicator, the color change from colorless to faint pink signals the end point. If a different indicator is used, different end point colors would be observed.

Similarly, the test for manganese relies on the production of the intensely colored permanganate ion. If the purple color of this ion develops, it is immediately known that the manganese standard (.05 mg/l) has been exceeded.

Another example of visual matching occurs in the use of Hydrion or multi-range pH paper. These papers have a color chart printed on the box. After the paper is immersed in the solution, the color of the paper is compared with the colors on the chart. The colors on the chart have been determined at given pH's, which are also printed on the chart. Thus, by comparing the color of the wet indicator strip with the color printed on the package, a reasonably good ($\pm$0.5 - $\pm$1.0 pH unit) estimate of the pH of the unknown can be made.

The color comparator method is used in the field determination of iron by the Hach method. In this method the orange color of the phenanthroline reagent is a function of the iron concentration in the sample. By comparing the color of the final solution, contained in a test tube, with the colors on a transparent color disc, the concentration of iron in the unknown can be determined.

A colorimeter is an electrically operated device which employs a photocell (in place of the eye) as the detector. The color intensity of the sample is electronically compared with the intensity of a suitable filter. The output is a scale reading calibrated in concentration of the parameter being read. The Hach colorimeter, along with the filters, is supplied with meter scales appropriate for the determination being made. Examples where this method is used are the SPADNS method for fluoride and the laboratory determination of chlorine residual.

ACIDS, ORGANIC
(Colorimetric Method)

Note: This colorimetric procedure is more precise and accurate than the old distillation procedure and about equal to the column chromatographic method. The test requires less than 30 minutes and is particularly advantageous where more than one digester is to be analyzed since several tests can be run simultaneously almost as easily as one test.

PRINCIPLE:

This procedure converts the organic acids (called volatile acids in the past because they were vaporized and separated by distillation) to colored materials that are measured by light absorption in a suitable instrument (colorimeter).

SAMPLE:

A very small portion of 0.5 ml is used for the test, therefore, a 6 oz. bottle is sufficient for organic acids and related tests.

EQUIPMENT:

1. Colorimeter or spectrophotometer.
2. Boiling water bath or kettle of boiling water on an electric hot plate or Bunsen burner.
3. Test tube rack to hold 3/4 inch test tubes.

REAGENTS:

The following reagents are necessary either to make reagent solutions or to use directly as purchased.

1. Sulfuric acid, H_2SO_4, concentrated, reagent grade.
2. Ethylene glycol, reagent grade.
3. Sodium hydroxide, NaOH, pellets, reagent grade.
4. Hydroxylamine hydrochloride, reagent grade.
5. Ferric chloride, $FeCL_3 \cdot 6H_2O$, lump, reagent grade.

SOLUTIONS:

1. Sulfuric acid, diluted. Mix equal volumes of reagent grade, concentrated sulfuric acid and distilled water. CAUTION: Always add acid to water--never water to acid.

2. Ethylene glycol, reagent grade. Use as purchased.

3. Sodium hydroxide 4.5N. Dissolve 90 g of sodium hydroxide pellets in distilled water and dilute up to 500 ml.

4. Hydroxylamine solution, 10%. Dissolve 10 g of hydroxylamine hydrochloride in distilled water and make up to 100 ml.

5. Ferric chloride reagent. Dissolve 20 g of ferric chloride hexahydrate ($FeCl_3 \cdot 6H_2O$) in distilled water, add 20 ml of concentrated sulfuric acid and dilute to 1 liter.

PROCEDURE:

1. Clarify a few milliliters of sample by filtration or centrifugation or both. (it is necessary to have a relatively clear sample since turbidity will interfere with light transmission.)

2. Provide test tubes in a rack--one for a blank and one for each sample.

3. Using clean pipets, carefully and exactly pipet 0.5 ml of distilled water into the blank tube and 0.5 ml sample into each sample tube. If the organic acids are more than 2000 mg/l, an aliquot diluted to 0.5 ml is used.

4. Add 1.5 ml ethylene glycol to each tube.

5. Add 0.2 ml of the diluted sulfuric acid (1-1) to each tube. Mix well by swirling tube.

6. Heat in a boiling water bath for exactly 3 minutes.

7. Cool immediately in cold water.

8. Add 0.5 ml hydroxylamine solution.

9. Add 2.0 ml of 4.5N sodium hydroxide. Mix well by swirling tube.

10. Add 10.0 ml ferric chloride solution.

11. Add 5.0 ml distilled water.

12. Stopper and invert to mix.

13. Let stand 5 minutes, unstoppered, for color development.

14. Read at 500 millimicrons after standing 5 minutes.

CALCULATION:

Calculate mg/l organic acids as acetic from calibration.

Note: A calibration curve can be made using a 2000 mg/l standard acetic acid solution. A series of 6 tubes are used containing 0.0, 0.1, 0.2, 0.3, 0.4, and 0.5 ml standard acetic acid made up to 0.5 ml volume with distilled water where necessary. The above step by step procedure is followed and percent transmission readings are plotted on semi-log graph paper.

REPORTING:

Report at mg/l organic acids as acetic acid.

COMMENT:

This method is suitable for the determination of organic acids in sewage treatment plant digesters and in raw sludge. It is particularly advantageous where several tests can be run simultaneously.

SIGNIFICANCE:

Organic acids are produced by the biological breakdown of the complex mass of sludge. The organic acids are converted to gas if proper conditions prevail for the methane bacteria. In such digesters which appear to operate properly, the organic acids have been found to vary from a low of approximately 100 mg/l to a high of near 1000 mg/l with the majority under 500 mg/l organic acids.

In digesters not operating properly, the organic acids may reach concentrations of several thousand mg/l. At these concentrations of organic acids, digestion is very poor, there is very little gas production and that produced is of very poor quality.

REFERENCES:

Montgomery, H. A. C., Dymock, Joan F., and Thom, N.S., "The Rapid Colorimetric Determination of Organic Acids and Their Salts in Sewage-sludge Liquor", Analyst, pp. 949-955, December, 1962.

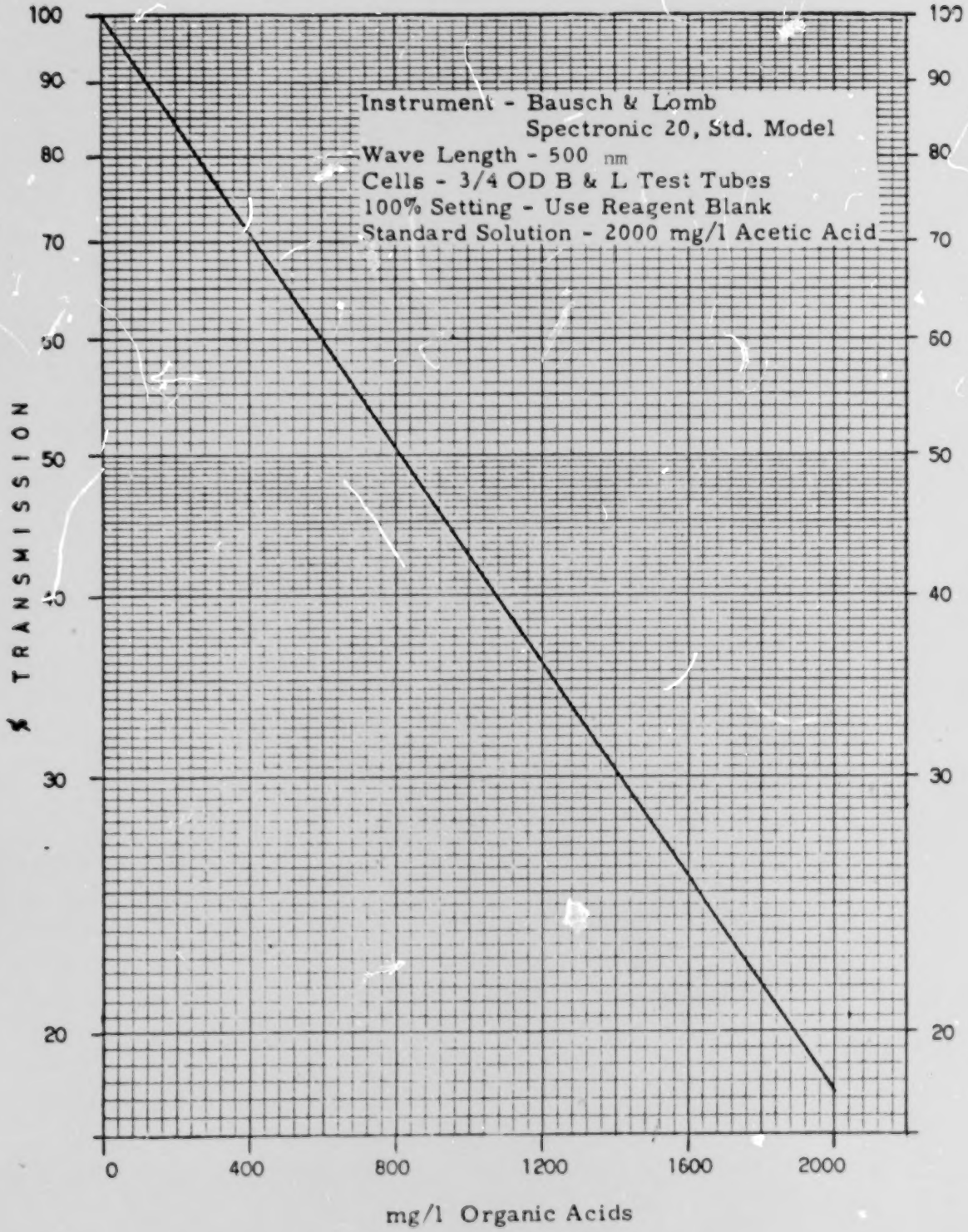
Mueller, H. F., Larson, T. E., and Ferretti, M., "Chromatographic Separation and Identification of Organic Acids", Analytical Chemistry, Vol. 32, pp. 687-690, May, 1960.

Sedlacek, M., "The Colorimetric Determination of Fatty Acids in Sludge and Sludge Waters", Chemical Abstracts, 62, 8822 (1965.)

CALIBRATION CURVE FOR ORGANIC ACIDS

COLORIMETRIC METHOD

(Each person must prepare one of these and check it periodically)



ACIDS, ORGANIC
(Column Chromatographic Method)

PRINCIPLE:

Organic acids are separated from inorganic acids and alkalies by placing an acidified sample on a short silicic acid column and eluting with a n-butanol-chloroform solvent. The organic acids are measured in the eluate by titration with standard NaOH.

SAMPLE:

A sample in a 6 oz. bottle is sufficient for organic acids and related tests.

MATERIALS:

1. Fume Hood.
2. Vacuum source.
3. Gooch crucibles, Coors No. 3 tail form, or special Kontes* 001489-49 Chromatographic column with extra coarse disc. (The Kontes chromatographic column has sufficient volume to hold all the solvent in one application. The Gooch crucible requires numerous applications of solvent.)
4. Crucible holder of #6 one-hole rubber stopper.
5. Filtering flask -- 250 ml.
6. Buret, 10 ml, and buret holder.
7. Pipets, 1 and 5 ml.
8. Graduate, 50 ml.
9. Erlenmeyer flasks, 125 ml.
10. Glass fiber filter paper 2.0 cm #X-934-AH. H. Reeve Angel and Company, Inc.
11. Funnel, 65 mm. short stem.
12. Filter paper, Whatman #2, 12.5 cm.

---

*Kontes of Illinois
1916 Greenleaf Street
Evanston, Illinois

REAGENTS:

1. Silicic acid: Mallinckrodt's Silicic Acid No. 2847 "specially prepared for chromatography." The silicic acid is dried at 105° and stored in a desiccator.

2. CB_{25} solvent: Mix 250 ml of n-butyl alcohol with 750 ml chloroform.

3. NaOH: 0.02 N NaOH protected from CO_2 absorption.

4. H_2SO_4: Approximately 10 N H_2SO_4.

5. Thymol blue indicator: 0.1 percent by weight in absolute methyl alcohol or ethyl alcohol.

6. Phenolphthalein indicator: 0.1 percent by weight in absolute methyl alcohol or ethyl alcohol.

7. Methyl alcohol: absolute.

PROCEDURE:

1. Filter through 12.5 cm #2 filter paper, sufficient sludge to obtain approximately 10 to 15 ml filtrate.

2. Use either a Gooch crucible or Kontes chromatographic column. If a Gooch crucible is used, place fiber filter pad on the bottom of the Gooch crucible and draw down by suction on a vacuum filter flask and then release vacuum. If the Kontes chromatographic column is used, no glass fiber pad is needed.

3. Remove column from vacuum filter flask and put 10 grams of dry silicic acid in the column tapping lightly to aid in packing.

4. Replace column on vacuum filter flask and apply vacuum to pack the silicic acid. It may be necessary to remove the column from the flask, tap again, replace on vacuum filter flask and re-apply vacuum in order to firmly pack the silicfc acid with no drawing away from the column wall.

5. Add one drop of thymol blue indicator to filtrate from Step #1.

6. Add 10 N H_2SO_4 drop-wise with mixing until sample is red to thymol blue.

7. Place 5.0 ml of acidified sample on the silicic acid in the column. Release vacuum as soon as sample is drawn into silicic acid.

8. With suction, draw CB_{25} solvent through the silicic acid into the filtering flask, keeping the column full until 50 ml have been added and drawn into the flask.

9. Remove filter flask, add 40 ml methyl alcohol and 5 drops of phenolphthalein to the eluate in the flask.

10. Titrate with 0.02 N NaOH to a pink end-point.

11. Run a blank titration on the solvents (approximately 45 ml CB_{25} and 40 ml methyl alcohol) and subtract from the above titration (Step #10) to obtain net ml used.

CALCULATION:

Organic acids in mg/liter as acetic = (ml of 0.02 N NaOH used on sample-ml used on blank) X 240.

COMMENT:

This method is suitable for the determination of organic acids in sewage treatment plant digesters and in raw sludge.

SIGNIFICANCE:

Organic acids are produced by the biological breakdown of the complex mass of sludge. The organic acids are converted to gas if proper conditions prevail for the methane bacteria. In such digesters which appear to operate properly, the organic acids have been found to vary from a low of approximately 100 mg/l to a high of near 1000 mg/l with the majority under 500 mg/l organic acids.

In digesters not operating properly, the organic acids may reach concentrations of several thousand mg/l. At these concentrations of organic acids, digestion is very poor, there is very little gas production and that produced is of very poor quality.

REFERENCES:

Mueller, H.F., Buswell, A.M., and Larson, T.E., "Chromatographic Determination of Volatile Acids," Sewage and Industrial Wastes, Vol. 28, pp. 255 to 259, (1956).

Etzel, J.E. and Pohland, F.G., "Volatile Acid Formation During Sludge Digestion," Public Works, pp. 105-08, (July 1960).

Pohland, F.G., and Dickson, B.H., "Organic Acids by Column Chromatography", Water Works and Wastes Engineering, pp. 54, 55 and 73, (July 1964).

Standard Methods For The Examination of Water and Wastewater, (13th Edition), American Public Health Association, New York, New York (1971).

Westerhold, A.F., "Organic Acids in Digester Liquor by Chromatography", Journal Water Pollution Control Federation, Vol. 35, No. 11, pp. 1431-1433, (1963).

ACIDS, VOLATILE
(Distillation Method)

PRINCIPLE:

Volatile acids are separated from the sample by distillation. The acids are measured in the distillate by titration with a standard sodium hydroxide solution.

SAMPLE:

A pint sample is sufficient for volatile acids and related tests.

APPARATUS:

1. Centrifuge or other means of clarifying liquid from the sample.
2. Distillation apparatus consisting of 500 ml round bottom distilling flask, condenser, adapter tube and ring stand support with ring and clamps.
3. Heat source--either a suitable electric heater or Fisher type of gas burner.
4. Buret.

REAGENTS:

1. Sulfuric acid, 1 + 1. (add 1 part conc. H_2SO_4 to 1 part distilled water by volume.)
2. Sodium hydroxide standard solution, 0.1N.
3. Phenolphthalein indicator solution. Dissolve 0.5 g phenolphthalein in 50 ml ethyl or methyl alcohol and add 50 ml distilled water. Add NaOH drop-wise until a faint pink color appears.
4. Hengar granules, plain not selenized, for use as boiling chips to promote smooth boiling.

PROCEDURE:

1. Centrifuge sufficient sample to get 100 ml (or suitable aliquot) of supernatant for distillation.
2. Place 100 ml (or aliquot) of supernatant in distillation flask.

3. Add 100 ml of distilled water, or if less than 100 ml sample was taken, the required amount to make a total of 200 ml.

4. Add 5 or 6 Hengar granules or boiling chips for smooth boiling.

5. Add 5 ml of 1 + 1 H_2SO_4.

6. Swirl flask to mix acid and sample.

7. Connect flask to condenser.

8. Distill at a rate of 5 ml per minute.

9. Collect 150 ml of distillate in a 250 ml graduated cylinder. Transfer, without loss, the entire distillate to a 250 ml Erlenmeyer flask.

10. Titrate with 0.1N NaOH using pehnolphthalein indicator. The end-point is the first pink coloration that persists for a short time. Titration at 90°C reduced carbon dioxide interference and produces a stable end-point.

CALCULATION:

$$\text{Volatile acids in mg/l as acetic} = \frac{\text{ml NaOH} \times 6000}{\text{ml sample} \times 0.7}$$

COMMENT:

This method is suitable for routire control purposes. It is not recommended for accurate work since it is assumed that only 70% of the volatile acids present in the samples will be found in the distillate. This factor has been found to vary considerably.

SIGNIFICANCE:

Volatile organic acids are produced by the viological breakdown of the complex mass of sludge. The volatile acids are converted to gas if proper conditions prevail for the methane bacteria. In such digesters which appear to operate properly, the volatile acids have been found to vary from a low of approximately 100 mg/l to a high of near 1000 mg/l with the majority under 500 mg/l volatile acids.

In digesters not operating properly, the volatile acids may reach concentrations of several thousand mg/l. At these concentrations of volatile acids, digestion is very poor, there is very little gas production and that produced is of very poor quality.

REFERENCE:

Standard Methods for the Examination of Water and Wastewater, (11th Edition), 1960, p. 422.

ALKALINITY
(For Use On Digester Supernatant)

PRINCIPLE:

Alkalinity is measured on a clarified digester supernatant sample by titration with a standard acid to a colorimetric end-point.

SAMPLE:

Use part of Volatile or Organic Acid sample.

REAGENTS:

1. Sulfuric acid standard solution 0.02N (1 ml = 1 mg alkalinity as $CaCO_3$).

2. Methyl purple indicator solution, Fleisher, pH range 4.8 - 5.4 for total alkalinity. (Many people use methyl orange indicator and refer to the alkalinity thus determined as M.O. alkalinity; however, methyl purple gives a much more easily observed color change (from green to gray to purple) than the color change produced by methyl orange).

PROCEDURE:

1. Pipet 10.0 ml (or aliquot) of filtered supernatant into a 125 ml Erlenmeyer flask. Dilute to 50 ml with distilled water.

2. Add 3 - 4 drops of methyl purple indicator. A green color should develop. (In some cases of acid digesters, there is little or no alkalinity with an accompanying low pH and a gray or purple color will develop.)

3. Fill the buret with 0.02 N H_2SO_4.

4. Record the reading.

5. Titrate with vigorous swirling of the sample through the development of the intermediate gray color to the development of a distinct purple end-point.

6. Read the buret and record final reading. Subtract the initial buret reading from the final reading to get the net ml of 0.02N H_2SO_4 used in the sample.

CALCULATION:

$$\text{mg/l total alkalinity} = \frac{\text{net ml of 0.02N acid} \times 1000}{\text{ml of sample used}}$$

SIGNIFICANCE:

Alkalinity refers to the quantity of basic compounds in aqueous solution which shift the pH value of the solution to the alkaline side of neutrality. These alkaline substances react with acids to produce neutral compounds.

REFERENCE:

Standard Methods For The Examination of Water and Wastewater (13th Edition), 1971, pp. 370-376.

CHLORINE, RESIDUAL
(Orthotolidine Method)

PRINCIPLE:

The addition of orthotolidine reagent to sewage containing chlorine produces a color proportional to the amount of chlorine present. The method is not specific for chlorine. Nitrites, organic matter and manganic manganese interfere.

SAMPLE:

At least 10 milliliters are required.

REAGENTS AND EQUIPMENT:

1. Orthotolidine reagent: Dissolve 1.35 g orthotolidine dihydrochloride in 500 ml distilled water. Add this solution, with constant stirring, to a mixture of 350 ml distilled water and 150 ml conc. HCl. This reagent should be stored in amber bottles preferably in the dark and protected always from direct sunlight. It is suggested that orthotolidine reagent be discarded after six months.

2. Chlorine comparator, turbidity compensating.

PROCEDURE:

1. Add a 10 ml sample of chlorinated sewage to a cell or test tube containing 1 ml orthotolidine reagent.

2. Mix, and if the temperature of the sample is less than 20°C, bring it to that temperature quickly after mixing, and hold in the dark for color development.

3. Read when the color intensity reaches its peak (usually in 3 - 5 minutes).

REPORTING:

Report as mg/l chlorine.

SIGNIFICANCE:

Because of organic matter and ammonia, residual chlorine exists in sewage in the combined state. The orthotolidine method measures the combined available chlorine.

REFERENCES:

Standard Methods For The Examination of Water and Wastewater (13th Edition) 1971, pp. 385-386.

CYANIDE
(Colorimetric Test)

PRINCIPLE:

The cyanogen halide produced by adding an excess of bromine to the sample reacts with a pyridine-benzidine reagent to form an orange color which may be measured colorimetrically at 480 mu. This method measures free cyanide and some of the complexes. For a measure of total cyanide, a surface distillation procedure is required before measurement by this method. Thiocyanates are an interference but can be eliminated by distillation.

SAMPLE:

Collect a 6 ounce sample. If it cannot be analyzed immediately, it should be preserved with NaOH by raising the pH to 11.0 or above. Usually two NaOH pellets are sufficient.

REAGENTS:

1. Phenolphthalein solution, 0.5 percent.
2. Phosphoric acid solution, 10 percent.
3. Bromine water, saturated.
4. Sodium arsenite solution, 2 percent.
5. N-butyl alcohol, reagent grade.
6. Pyridine solution: Add 2 ml conc. HCl to 25 ml pyridine. Dilute to 100 ml.
7. Benzidine di-hydrochloride, 2 percent aqueous.
8. Potassium cyanide stock solution, 1000 mg/l: In a volumetric flask dissolve 2.51 g KCN, reagent grade, in 1000 ml water. For the greatest accuracy, this stock solution should be standardized by the modified Liebig method. CAUTION: Avoid ingestion--toxic.
9. Potassium cyanide standard solution (1 ml = 1 microgram CN^-). Dilute 10 ml stock cyanide solution to 1 liter with distilled water, mix and from this dilution make a second dilution of 10 ml to 100 ml. (1 ml = 1 microgram CN^-). Use 10 ml volumetric pipets to effect the transfer, and volumetric flasks in which to make the dilutions.

CALIBRATION:

1. From the standard KCN solution containing 1 microgram per ml as prepared in Step 9 above, make a series of standards containing 0,1,2,3,4 and 5 micrograms of CN^-. Make each standard up to 10 ml with distilled water, using volumetric glassware.

2. Follow the steps listed under Procedure to develop the color.

3. Prepare a calibration curve by plotting the percent transmittance for each standard against the micrograms of cyanide in that standard. The use of semi-logarithmic graph paper is helpful because all points should fall on a straight line. If ordinary graph paper is used, it is necessary to either read absorbance from the instrument or calculate absorbance in order to get a straight line.

PROCEDURE:

1. Set up a series of test tubes (25 x 150 mm) in two rows in a test tube rack. Each sample and blank requires two tubes.

2. Measure 10 ml distilled water into the first two tubes for reagent blanks.

3. Measure two 10 ml or appropriate aliquots of sample into two test tubes for the first sample and repeat this for each succeeding sample. (Dilute to 10 ml if less than 10 ml aliquot taken.)

4. Using the first tube in each set, determine the amount of phosphoric acid required to neutralize to approximately pH 8, with phenolphthalein as an indicator. To the second tube in each set, add a like amount of phosphoric acid and then 2 drops in excess to lower the pH. Discard the first row of tubes.

5. Add bromine water drop-wise to each tube until a slight excess is indicated by a persistent yellow color.

6. Add 2 percent sodium arsenite drop-wise to each tube in order to destroy the bromine color. Add 1 drop in excess.

7. Add 10 ml n-butyl alcohol to each tube, stopper and shake the tube.

8. Add 5.3 ml pyridine-benzidine reagent (mix 5 ml pyridine solution with 0.3 ml benzidine solution just before using) to each of the treated samples and to the alcohol blank.

9. Stopper and shake vigorously.

10. Allow 15 minutes for color development. (Cyanide is indicated by a brownish-yellow color in the upper alcohol layer).

11. Transfer some of the alcohol layer from the reagent blank to the instrument cell (usually a 1 cm cell is best) and set the instrument for 100 percent transmittance at 480 mu.

12. Transfer some of the alcohol layer of the sample to a second cell and read percent transmittance.

13. Calculate the amount of CN^- present from the calibration curve.

REPORTING:

Report as mg/l CN.

COMMENT:

Extreme caution should be exercised in the handling of all standard solutions, as well as any samples of unknown concentration of cyanide.

DO NOT USE MOUTH SUCTION ON ANY PIPET.

SIGNIFICANCE:

The PCB has placed an effective limit of 0.025 mg/l on the amount of cyanide which may be contained in water.

REFERENCES:

Nusbaum, I., Skupeko, P., "Determination of Cyanide in Sewage and Polluted Waters", Sewage and Industrial Wastes 23, 7 875-879 (1951).

Lancy, L.E., "Non-referee Method for Cyanides Amenable to Alkaline Chlorination in Industrial Waste Water". Private communication from Dr. L.E. Lancy of Lancy Laboratories, Inc. (1963).

Standard Methods for The Examination of Water and Wastewater (13 Edition) 1971 pp. 397-406.

SECTION 8 MISSING FROM DOCUMENT PRIOR
TO BEING SHIPPED TO EDRS FOR FILMING.

BEST COPY AVAILABLE

BIOCHEMICAL OXYGEN DEMAND (BOD)
(Graduate Dilution Method)

PRINCIPLE:

The biochemical oxygen demand (BOD) of sewage, sewage effluents, polluted waters or industrial wastes is the quantity of dissolved oxygen, in mg/liter, required during stabilization of the decomposable organic matter by aerobic biochemical action. Determination of this quantity is accomplished by diluting suitable portions of the sample with water saturated with oxygen and measuring the dissolved oxygen in the sample and in the dilution water blank immediately and in the mixture after a period of 5 days incubation at 20°C.

SAMPLE:

One quart is required.

REAGENTS:

1. All reagents necessary for the determination of DO.
2. Ferric chloride solution: 0.25 g/l $FeCl_3 \cdot 6H_2O$.
3. Calcium chloride solution: 27.5 g/l anhydrous $CaCl_2$.
4. Magnesium sulfate solution: 22.5 g/l $MgSO_4 \cdot 7H_2O$.
5. Phosphate buffer solution: Dissolve 8.5 g monobasic potassium acid phosphate, KH_2PO_4; 21.8 g dibasic potassium acid phosphate, K_2HPO_4; and 33.4 g diabasic sodium acid phosphate, $Na_2HPO_4 \cdot 9H_2O$; in 500 ml of distilled water. Then add 1.7 g ammonium chloride, NH_4Cl, and make to 1 liter. The pH of the solution should be 7.2 without further adjustment.
6. Seeding material: In many cases, a satisfactory seed may be obtained by using the supernatant from settled domestic sewage which has been stored for 24 to 36 hours at 20°C. Many industrial wastes contain organic compounds which are not amenable to oxidation by domestic sewage seed. In these cases, receiving water collected two to five miles below the point of discharge of the particular waste will undoubtedly give the best results. Experimentation with any particular seed will be the only means of determining the application of the seed for any given waste. Quantity must also be determined in this matter. Five to ten ml of settled raw sewage per 5 gal. of dilution water is suggested for the initial application of seed.

7. Distilled or de-ionized water: This water should be of the highest quality, containing no material toxic to the organisms found in the seed or in the waste itself. Copper and chlorine should be absent, with an allowable maximum of 0.01 mg/l copper. If any doubt exists regarding the suitability of the water, controls should be run by the procedure using a synthetic solution of known BOD. A 300 mg/l glucose solution should show a BOD of 224 $\pm$ 10 mg/l.

8. Dilution water: To five gallons of this water, previously stoppered with a cotton plug and aged for at least 2 weeks in darkness, add 20 ml each of calcium chloride solution, magnesium sulfate solution and phosphate buffer. In addition, add 10 ml ferric chloride solution and the amount of seed which has been determined by experimentation. Mix and allow to stand in the BOD incubator for at least a week before use. Stability of the dilution water and suitability for use after stabilization may be checked as follows:

   Into two BOD bottles (APHA) siphon, with a minimum of aeration, two like samples. Perform a dissolved oxygen determination on one of the bottles and incubate the second for five days at 20°C. If the dissolved oxygen of the dilution water falls below 7.5 mg/l, it may be aerated to bring the level to that of saturation. If the dissolved oxygen of the dilution water indicates that it is super-saturated, it must be de-aerated before it is used.

   At the end of the incubation period, perform a DO test on the second portion of the dilution water. The difference in DO for the initial and incubated sample will be the BOD of the dilution water itself which should be less than 0.2 mg/l.

PROCEDURE:

In BOD work, some experience or guidance is necessary in determining what dilution to set up for the various types of samples. With a knowledge of the source of the sample and an observation of the odor, turbidity and suspended solids, one can estimate a probable BOD and select suitable dilutions to cover the estimated BOD. It is desirable to make two dilutions on each sample.

1. Fill two BOD bottles with dilution water, using a siphon and keeping aeration at a minimum. Determine the DO of one bottle and incubate the second.

2. Determine the DO of the original sample, taking care not to aerate the sample in the process.

3. To a 1 liter graduate, add the amount of well-mixed sample required for the selected dilution (See "Comment").

Dilute to 1 liter with prepared dilution water and mix well without aeration using a plunger-type stirrer.

4. Transfer the diluted sample to a BOD bottle without aeration. Stopper the bottle, filling the collar with water, and incubate. Using a siphon, discard mixture in excess of 500 ml.

5. Further dilutions should be made by adding dilution water equal to volume remaining in the graduate from Step 4. This is in effect halving the concentration. When the dilution and mixing are completed, repeat Step 4.

   NOTE: Repeat the dilution procedure as often as necessary to cover any suspected deviation from the estimated BOD.

6. When all dilutions are completed, fill an additional bottle with the dilution water and incubate it along with the sample dilutions for a period of 5 days at 20°C.

7. At the end of the incubation period, remove the samples from the incubator and determine the remaining dissolved oxygen for each dilution, as well as for the two dilution water blanks. Dissolved oxygen depletions in the range of 40 to 90 percent will give the most accurate values when the calculation of the BOD is performed.

COMMENT:

If the sample is extremely alkaline or high in acidity, the pH must be adjusted before dilution.

Table of BOD Dilutions and Factors

BOD Range	Dilution Desired %	Volume of Sample	Factor or Multiplier
0-5	100	1000	1
4-10	50	500	2
8-20	25	250	4
20-50	10	100	10
40-100	5	50	20
80-200	2.5	25	40
200-500	1.0	10	100

CALCULATION:

$$BOD = (W-D) \times \frac{100}{P} + S-W$$

W = DO in dilution water blank after incubation.

D = DO in sample dilution after incubation.

S = DO in sample before dilution.

P = Percent of sample in dilution.

REPORTING:

Report as mg/l BOD (5 days @ 20°C).

SIGNIFICANCE:

The biochemical oxygen demand of sewage, polluted waters, or industrial wastes is exerted by three classes of materials: (1) carbonaceous organic matter, such as cellulose, starch, sugar, fat; (2) oxidizable nitrogen derived from urea, ammonia, nitrite, and organic nitrogen compounds; and (3) reducing compounds such as ferrous iron, sulfite and sulfide.

With domestic sewage, the BOD test measures the first class of materials. The test may not be significant if the sample contains the second or third class of materials.

REFERENCES:

Standard Methods For The Examination of Water and Wastewater, 13th Edition, 1971; pp 489-495 with modifications by the Illinois Environmental Protection Agency.

Ibid, 9th Edition, 1946; pp 139-144.

BIOCHEMICAL OXYGEN DEMAND (BOD)
(Simplified Non-standard Method)

PROCEDURE:

In BOD work, some experience or guidance is necessary in determining what dilutions to set up for the various types of samples. With a knowledge of the source of the sample and an observation of the odor, turbidity, and suspended solids, one can estimate a probable BOD and select suitable dilutions to cover the estimated BOD. The following table may be consulted to determine the volume of sample and volume of dilution water to be used. It is desirable to make two dilutions at different concentrations on each sample.

BOD Range	Dilution Desired	Volume of Sample	Volume of Dilution Water	Total Volume	Factor or Multiplier
0-5	100	1000	0	1000	1
4-10	50	500	500	1000	2
8-20	25	250	750	1000	4
20-50	10	100	900	1000	10
40-100	5	50	950	1000	20
80-200	2.5	25	975	1000	40
200-500	1.0	10	990	1000	100

1. Measure the correct amount of well-mixed sample and add to a 100 ml graduated cylinder or to a 2-quart bottle.

2. Measure the correct amount of dilution water (enough to make the total volume of sample and dilution water equal to 1000 ml). Add this to the measured sample.

3. If a 1000 ml graduated cylinder is used, mix the contents with a stirring rod. If using a bottle, stopper the bottle and mix the contents by shaking the bottle.

4. Allow the mixture to stand for a minute to eliminate air bubbles.

5. Transfer the mixture carefully to two duplicate, clean, B.O.D. bottles. Insert stoppers in the bottles. (To insure getting representative portions in each bottle, it is preferable to fill the first bottle half full, then fill the second bottle full and finally fill the first bottle full. This should tend to average out any difference due to suspended solids.)

6. Run the D.O. test on one of these bottles. Record the results as Initial D.O.

7. Complete the water seal on the second bottle, and place in incubator for 5 days.

8. At the end of five days, run the D.O. test and record the result as Final D.O.

9. Calculate the BOD of the original sample, using the correct multiplier or factor for the dilution used.

Calculation of BOD:

Determine factor or multiplier from dilution table.

BOD = Difference x Factor

Example:

25% Dilution:

Initial D.O.	8.5
Final D.O.	2.0
Difference	6.5

25% dilution = factor of 4

BOD = 6.5 x 4 = 26.0

REPORTING:

Report as mg/liter BOD (5 day @ 20°C).

COMMENT:

This simplified non-standard method is included as a method for those who want a method more simple than the preferred graduate dilution method.

Table for Recording BOD Results

Source of Sample	Percent of Sewage in the Dilution	Initial D.O. in the Dilution	Final D.O. in the Dilution	Difference	Factor	5 Day BOD

DISSOLVED OXYGEN (D.O.)

PRINCIPLE:

The sample is collected in a glass-stoppered D.O. bottle without aeration. Immediately after collection, the sample is allowed to react with manganous sulfate in the presence of alkaline solution of iodide and sodium azide. The azide removes nitrite interference. A brown-colored flocculant precipitate forms when oxygen is present. On acidification with sulfuric acid the brown-colored floc reacts with the iodide to release iodine in a quantity equivalent to the dissolved oxygen content of the sample. The liberated iodine is then titrated with a standard solution of sodium thiosulfate.

SAMPLE:

The sample should be collected in a standard dissolved oxygen bottle using an appropriate dissolved oxygen sampler to avoid aeration.

REAGENTS:

Prepared reagents meeting APHA specifications can be purchased from laboratory supply houses or they can be made as follows:

1. Manganous sulfate solution: Dissolve 364 g $MnSO_4 \cdot H_2O$ in distilled water and filter. Dilute to 1 liter. (Specific gravity should be 1.270) The solution should not liberate more than a trace of iodine when added to an acidified solution of potassium iodide.

2. Alkaline iodide-azide solution: Dissolve separately 500 g NaOH and 150 g KI in distilled water and dilute to 1 liter. To this solution add 10 g NaN_3 dissolved in 40 ml distilled water. This reagent should not give a color with starch indicator when diluted and acidified.

3. Sulfuric acid, conc. H_2SO_4.

4. Starch indicator solution: Suspend 5 g of powdered potato starch in a small amount of distilled water and make to approximately 750 ml. Dissolve 12.5 g NaOH in 100 ml distilled water and stir into the starch suspension until a thick, sirupy, almost clear solution is obtained. Allow to stand one hour or more. Neutralize with approximately 25 ml conc. HCl using a pH meter to determine

the end-point. Do not overrun the end-point. For preservative, add 8 g sodium propionate and 4 g sodium azide. Dissolve each in 25 ml of distilled water and add to the starch solution. Dilute to 1 liter.

5. Sodium thiosulfate solution, 0.10N: Dissolve 24.82 g $Na_2S_2O_3 \cdot 5H_2O$ in boiled and cooled distilled water, preserve with 1 g NaOH and dilute to 1000 ml. Standardize with biniodate solution (a).

   a. Standard potassium biniodate solution: 0.10N: Prepare a stock equivalent to 0.10 N by dissolving 3.249 g $KH(IO_3)_2$ in distilled water and diluting to 1 liter.

   b. Standardization of sodium thiosulfate: Dissolve 2 g KI (iodate-free) in an Erlenmeyer flask in 100 to 150 ml distilled water.

      Add 10 ml (1 ml H_2SO_4 + 9 ml distilled H_2O) followed by exactly 20 ml standard biniodate solution. Dilute to about 200 ml and titrate the liberated iodine with the approximate 0.1 N thiosulfate to a pale straw color. Add 1 ml of starch indicator and titrate to disappearance of the blue color. Calculate normality and adjust to 0.10 N if necessary.

6. Standard sodium thiosulfate solution, 0.025 N: Prepare by diluting 250 ml of 0.10 N stock solution to 1 liter.

PROCEDURE:

1. Collect sample, filling D.O. bottle full to top.
2. Replace stopper and discard excess water.
3. Remove stopper.
4. Add 2 ml manganous sulfate solution and 2 ml alkaline potassium iodide solution. Place delivery tip of pipet below the surface of the water in the sample bottle.
5. Replace stopper giving it a slight twist to seat it well and rinse bottle with tap water.
6. Shake well by inversion of the bottle.
7. Allow the precipitate to settle slightly. Then shake by inversion again.

8. After precipitate has settled in lower half of bottle, remove the stopper.

9. Add 2 ml of concentrated sulfuric acid with the tip of the pipet above the surface of the sample but touching the inside neck of the bottle.

10. Replace stopper, rinse with tap water, and shake sample to distribute the iodine uniformly throughout the bottle.

11. Shake the sample once more and measure 203 ml of the iodine solution with a measuring flask. (Cut off volumetric flask may be used).

12. Discard the excess iodine solution and pour the measured portion back into the original bottle.

13. Proceed at once with the titration.

14. Fill buret with 0.025 N (N/40) thiosulfate solution.

15. Read buret and record reading.

16. Add thiosulfate from the buret in small amounts. Swirl the bottle and sample after each addition.

17. Continue the titration until the color of the sample is that of light straw.

18. Add 1 ml of starch indicator. The color of the sample will change to blue.

19. Continue the titration, using care not to overrun the end-point, which is the disappearance of the blue color.

20. Read the buret at the end-point and record the reading.

21. Subtract the reading at the start (step 15) from the reading at the end (step 20). The difference is the volume of N/40 thiosulfate required for 200 ml of the original sample.

22. This difference is equal to the dissolved oxygen of the sample in terms of milligrams per liter (mg/l).

REPORTING:

Report as mg/liter dissolved oxygen.

SIGNIFICANCE:

The test for dissolved oxygen (D.O.) is one of the most valuable single analytical measures of the condition of water with respect to pollution. It is also the basic part of the biochemical oxygen demand test.

A minimum D.O. of 5 mg/l is necessary for normal fish life and growth, although fish survive at 3 mg/l or less depending on the species.

REFERENCE:

Standard Methods For The Examination of Water and Wastewater (13 Edition), 1971, pp. 474-488.

DATA SHEET FOR DISSOLVED OXYGEN

SAMPLE	Buret Reading		ml Difference	mg/liter Dissolved Oxygen
	Final (Step 20)	Initial (Step 15)		
1.				
2.				
3.				
4.				
5.				
6.				
7.				
8.				

ml difference = mg/l D.O., when 203 ml of the sample is titrated with 0.025 N (N/40) thiosulfate.

DISSOLVED OXYGEN
(Copper sulfate-sulfamic modification)

PRINCIPLE:

This modification is used for biological flocs such as activated sludge mixtures which have high oxygen utilization rates. The copper sulfate-sulfamic acid accomplishes a twofold purpose. It stops the oxygen utilization immediately and it causes the organic material to precipitate producing a clear supernatant for testing.

This method is quite useful; however, dissolved oxygen meters which are capable of direct measurements in the aeration tank are to be preferred.

APPARATUS:

1. All equipment used in the DO test.
2. Siphon.
3. One quart wide mouth bottle with large rubber stopper to fit or 1 liter glass stoppered bottle.
4. DO bottles.

REAGENTS:

1. All the reagents required for the dissolved oxygen test.
2. Copper sulfate-sulfamic acid inhibitor solution: Dissolve 32 g technical grade sulfamic acid, NH_2SO_2OH, without heat, in 475 ml distilled water. Dissolve 50 g copper sulfate, $CuSO_4 \cdot 5H_2O$, in 500 ml distilled water. Mix the two solutions together and add 25 ml of conc. acetic acid.

PROCEDURE:

1. Add 10 ml copper sulfate-sulfamic acid inhibitor.
2. Insert bottle in sampler designed so that the bottle fills from a tube near the bottom and overflows only 25 to 50% of bottle capacity.
3. Collect the sample, stopper and mix by inversion.
4. Allow the solids to settle.

5. Siphon the relatively clear supernatant liquor into a DO bottle.

6. Continue the DO analysis immediately using the azide modification of the DO procedure as detailed in this manual.

SIGNIFICANCE:

This modification of the DO test is used to permit the measurement of dissolved oxygen to determine the adequacy of aeration of activated sludge.

REFERENCE:

Standard Methods for the Examination of Water and Wastewater, 13th Edition, 1971, pp. 483-484.

OXYGEN DEMAND INDEX

Two procedures are provided. The reagents for the original ODI procedure were based on published information in "Analytical Chemistry" on the elimination of chloride interference in the COD test. This necessitated the making of two complex chemical reagents in order to hold the operational steps to a minimum. These reagents are specialized and less readily available than most reagents.

After the introduction of the ODI procedure in the February, 1965 issue of "The Digester", the 12th Edition of "Standard Methods" (1965) was published with a simpler method of addition of reagents to eliminate chloride intereference. This improved technique made it possible to use "Standard Methods' " COD reagents in the ODI test with only slight modifications in ODI procedure. The second ODI procedure employs this method of elimination of chloride interference with regular COD reagents.

Both procedures, if followed carefully, should give identical results. The advantage of the second method is largely the lower cost and ease of making or purchasing reagents.

PRINCIPLE:

This test is a modification of the dichromate oxygen demand test. The dichromate is reduced from the yellow hexavalent to the green trivalent state by organic material in a sample. The amount of green color produced is measured colorimetrically to give an approximate measure of sample strength in a short period of time.

SAMPLE:

A sample of 25 ml is sufficient.

EQUIPMENT:

1. Electrically heated water bath. (A kettle of water boiling on an electric hot plate or Bunsen burner is satisfactory.)
2. Colorimeter or spectrophotometer with one inch test tube cell or equal.
3. Test tube rack to hold 1 inch test tubes, (made locally).

REAGENTS:

1. Potassium dichromate, A.R. ($K_2Cr_2O_7$).

2. Mercuric sulfate, A.R. ($HgSO_4$).

3. Dextrose (glucose) crystal, reagent or pure bacterial grade, anhydrous.

4. Silver sulfate, A.R. (Ag_2SO_4).

5. Sulfuric acid, conc. A.R. (H_2SO_4).

SOLUTIONS:

1. Standard 0.25 N dichromate solution. Dissolve 12.259 g $K_2Cr_2O_7$ reagent grade (dried at 103°C for 2 hours) in distilled water and dilute to 1000 ml.

2. Reagent A: Add carefully 125 ml conc. H_2SO_4 to 375 ml of 0.25 N dichromate solution contained in a 500 ml pyrex bottle.

3. Reagent B: Add 7.5 g Ag_2SO_4 to 700 ml conc. H_2SO_4 contained in a 1 liter pyrex bottle.

4. Standard glucose solution used for making calibration curve. Dissolve 0.600 g glucose (dried at 103°C for 1 hour) in distilled water and make up to 1000 ml. (This solution should have a BOD of 448 $\pm$ 20 mg/l; see "Standard Methods," Twelfth Edition, pages 418-419. One ml of this solution diluted to 5.0 ml has an Oxygen Demand Index (ODI) value of 90 based on BOD tests.)

PROCEDURE: (Using ODI reagents)

1. Pipet 5.0 ml of distilled water into a 25 mm x 150 mm test tube for a blank. Use special rack to hold tubes.

2. Pipet 5.0 ml sample into a second tube.

3. Add 2.0 ml of Reagent A to each tube.

4. Add 0.1 g $HgSO_4$ (approximately, with a measuring spoon) to each tube.

5. Mix well (all $HgSO_4$ may not dissolve).

6. Add 7.0 ml Reagent B to each tube. (CAUTION: Strong Acid).

7. Mix well. (Be sure sample and regents are well mixed.)

8. Place rack containing blank and sample tubes in boiling water bath for 20 minutes.

9. Remove, cool in water or let stand to cool. This also allows time for $HgSO_4$ and other suspended material to settle.

10. Measure the % transmission at 600 mu, using the reagent blank 100 percent line.

11. Calculate ODI value from a graph prepared by running 0.0, 1.0, 2.0, 3.0, 4.0, and 5.0 ml volumes of 600 mg/l glucose solution. (All standards of less than 5.0 ml made up to 5.0 ml test volume with distilled water. 1.0 ml diluted to 5.0 ml has an ODI value of 90.

Solutions and Procedure for Alternate Method

SOLUTIONS:

1. Standard 0.25 N dichromate solution. Dissolve 12.259 g $K_2Cr_2O_7$ reagent grade (dried at 103°C for 2 hours) in distilled water and dilute to 1000 ml.

2. Sulfuric acid, silver sulfate reagent. Add 22 g silver sulfate (Ag_2SO_4) per 9 lb bottle of conc. sulfuric acid. Invert bottle ocasionally to aid in dissolution (1 to 2 days may be required).

3. Standard glucose solution used for making calibration curve. Dissolve 0.600 g glucose (dried at 103°C for 1 hour) in distilled water and make up to 1000 ml. (This solution should have a BOD of 448 $\pm$ 20 mg/l; see "Standard Methods", 12th Edition, pages 418-419. One ml of this solution diluted to 5.0 ml has an Oxygen Demand Index (ODI) value of 90 based on BOD tests.)

PROCEDURE: (Using COD reagents)

1. Place 25 mm x 150 mm test tubes in rack (1 for blank and 1 for each sample).

2. Add 0.1 g mercuric sulfate powder (approximately, with a Hach Chemical Company #510 or equal measuring spoon) to each tube.

3. Add, with pipet, 5.0 ml distilled water into blank tube.

4. Add, with pipet, 5.0 ml sample (or aliquot made up to 5.0 ml) into each sample tube and swirl to mix.

5. Add exactly, with pipet, 1.5 ml of 0.25 N dichromate solution.

6. Add carefully 7.5 ml of the sufuric acid-silver sulfate reagent.

7. Mix well by swirling tube. If a slight precipitate remains, it does not adversely affect the determination. (Be sure sample and reagents are well mixed).

8. Place rack containing blank and sample tubes in boiling water bath for 20 minutes.

9. Remove, cool in water or let stand to cool. This also allows time for $HgSO_4$ and other suspended material to settle.

10. Measure the % transmission at 600 mu, using the reagent blank to set the 100 percent line.

11. Calculate ODI value from graph prepared by running 0.0, 1.0, 2.0, 3.0, 4.0, and 5.0 ml volumes of 600 mg/l glucose solution. (All standards of less than 5.0 ml are to be made up to 5.0 ml test volume with distilled water. 1.0 ml diluted to 5.0 ml has an ODI volume of 90.)

REPORTING:

Report as ODI.

SIGNIFICANCE:

On samples containing bio-degradable material the ODI values should be roughly equivalent to BOD values. Samples containing nonbio-degradable material oxidizable by dichromate may give high values.

REFERENCES:

Moore, W.A., Kroner, R.C. and Ruchhoft, C.C., "Dichromate Reflux Method for Determination of Oxygen Consumed.", Anal. Chem. 21:953 (1949).

Moore, W.A., Ludzack, F.J., and Ruchhoft, C.C., "Determination of Oxygen Consumed Values of Organic Wastes", Anal. Chem. 23:1297 (1951).

Sawyer, C.N., et al., "Primary Standards for BOD Work", Sewage and Ind. Wastes, 22:26 (1950).

Dobbs, R.A. and Williams, R.T., "Elimination of Chloride Interference in the Chemical Oxygen Demand Test", Anal. Chem., 35:1064 (1963).

Westerhold, A.F., "Oxygen Demand Index", presented at Annual Operators Conference, Springfield, Illinois, April 8, 1964.

Standard Methods for the Examination of Water and Wastewater, 12th Edition, 1965.

Ibid, (13th Edition) 1971.

Shriver, L.E. and Young, J.C., "Oxygen Demand Index as a Rapid Estimate of Biochemical Oxygen Demand," JWPCF, 44:2140 (1972).

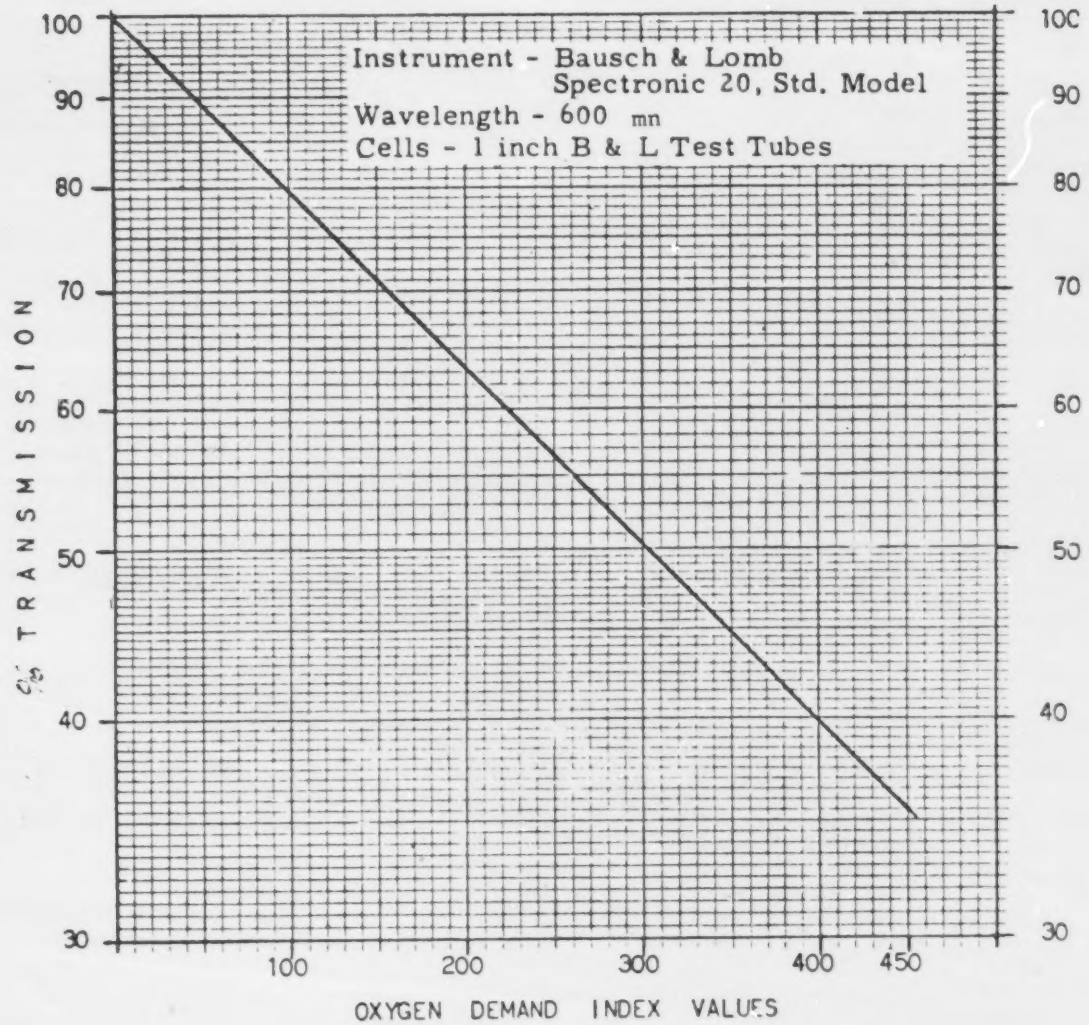
EXAMPLE OF OXYGEN DEMAND INDEX STANDARDIZATION TABLE
(Based on Following Calibration Curve)

To use this table, find the percent transmission of the sample in the %T column and read the ODI value in the ODI column.

%T	ODI	%T	ODI
98	10	66	180
96	20	63	200
93	30	60	225
91	40	56	250
89	50	53	275
87	60	50	300
85	70	47	325
83	80	44	350
81	90	42	375
79	100	40	400
76	120	38	425
72	140	36	450
69	160		

* * * * * * * * * * * * * * * * * *

EXAMPLE OF CALIBRATION CURVE FOR THE ODI TEST
(Each person must prepare one of these & check it periodically)

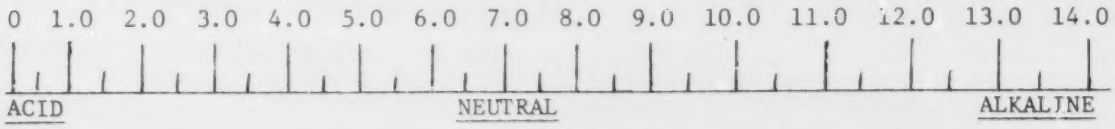


pH DETERMINATION

The symbol pH represents the value for the hydrogen ion concentration of a solution. By definition, pH is considered to be the negative logarithm (to the base 10) in moles per liter of the hydrogen ion concentration or activity of a solution (the p refers to the exponent or power and the H refers to Hydrogen).

The above description of pH is much too technical and considerably beyond the needs of the average sewage plant operator. The following "down to earth" material adapted from "Modern pH and Chlorine Control" by W.A. Taylor and Company, "Tools for Science" by Coleman Instruments and "Standard Methods for the Examination of Water and Wastewater" should give an insight into the practical side of pH.

Making a pH determination is almost as simple as taking a temperature with a thermometer. Intensity of heat is expressed as degrees on the thermometer scale. Similarly the pH scale is used to denote intensity of acidity and alkalinity. It is unnecessary to know the meaning of the term pH to make accurate determinations of intensity of acidity and alkalinity. pH is a numerical scale for expressing the intensity of acidity or alkalinity.



The numbers 0 to 14, as shown on the scale, are used to express pH values; that is, intensity of acidity and alkalinity. The value pH 7.0, half-way between 0 and 14, is the neutral point. A solution having a pH of 7.0 is neither acid nor alkaline. The numbers below 7.0 denote acidity, intensity of acidity INCREASING as the numbers DECREASE. Thus a solution of pH 6.4 is very slightly acid, one of pH 6.0 is more intensely acid and one of pH 4.6 is still more intensely acid. The numbers between 7.0 and 14.0 are used to denote alkalinity, the intensity of alkalinity INCREASING as the numbers INCREASE. Thus a solution of pH 7.6 is very slightly alkaline, one of pH 8.0 is more intensely alkaline and one of pH 9.2 is still more intensely aklaline. These numbers represent absolutely definite degrees of acidity and alkalinity and therefore a statement such as "acidify to pH 5.6" or "make alkaline to pH 9.4" has a very definite meaning which cannot be expressed by the terms "slightly or strongly acid or alkaline."

A change in pH represents a much larger change in intensity of acidity or alkalinity than would be expected from the pH values since a change of 1.0 pH unit represents a change of 10 in intensity of acidity or alkalinity. This is illustrated by the following table.

pH Value	Values Showing Intensity	
0	10,000,000	Acid
1	1,000,000	
2	100,000	
3	10,000	
4	1,000	
5	100	
6	10	
7	1	Neutral
8	10	
9	100	
10	1,000	
11	10,000	
12	100,000	
13	1,000,000	
14	10,000,000	Alkaline

There are two general methods of pH measurement, the electrometric and the colorimetric. In the colorimetric method an indicator is added to the sample and a color is produced characteristic of the pH of the sample. "Standard Methods" no longer recommends the colorimetric procedure because of: "Interference contributed by color, turbidity, high saline content, colloidal matter, free chlorine, and variou oxidants and reductants. The indicators are subject to deterioration, as are the color standards with which they are compared. Moreover, no single indicator encompasses the pH range of interest in water." The electrometric method is now considered the standard procedure.

In the electrometric method, the pH is determined by measuring, with a potentiometer (millivolt meter), the voltage produced by two electrodes both in contact with the solution. The voltage of one (calomel) electrode is fixed and known. The voltage of the other (glass) electrode varies with the pH of the sample. The electrometric method is possible because certain glasses possess the property that: A thin layer of glass in contact with a liquid will develop, between its inner and outer surface, a difference of voltage that varies with the pH of the liquid. The glass electrode is a device constructed to take advantage of the peculiarity of this special glass and to make possible the measurement of these voltages that result from contact with different liquids. The voltages produced by these glass electrodes are so small that solid state circuits are used in pH meters for amplication before the voltage is fed to a meter calibrated in pH.

Because of the differences between the many makes and models of pH equipment, it is impossible to give instructions for the operation of all pH meters and colorimetric comparators. In each case, the manufacturer's instructions must be followed. All pH meters must be checked daily with standard buffer solutions before use. Periodically during use rechecks must be made. The electrodes must be carefully rinsed between tests so that there is no carry over from one test to the next.

pH IN PLAIN LANGUAGE

by Joseph E. Nelson
Director of Research
Chemtrix, Inc., Hillsboro, Oregon 97123

To understand and learn about pH measurements is not difficult as long as we stick to fundamentals. That is, let us be concerned with the question, "What is the pH of my solution?", and then we can think of the instruments and techniques as tools to help us get the answer.

In plain language we'll discuss what pH means, why it is important and the results that you may expect to get from reading this paper.

If you can study this paper and at the same time have an operating pH meter in front of you, the results will be even more dramatic. Here you'll read about it, see it, use your hands to make it work, and finally get the results, all in one tremendous learning effort.

Our format is simple - each subject heading asks a question, and the paragraphs that follow provide the answer.

To get off to a good start and give you some incentive, we'll begin with a look at why pH is important.

WHY IS pH IMPORTANT?

If the pH of the blood in your body were lowered one unit, you would die. Living things grow and survive in a particular pH environment and when the pH is not correct their growth and survival are threatened. For example, wheat, corn and other foodstuffs grow best in soil of a particular pH. To get the greatest yield, the farmer must condition his soil to achieve the proper pH. This explains, in part, why the yield per acre has increased in recent years since soil science has shown the farmer how to provide optimum conditions for best growth.

Here's a list of pH important areas.

1. Drinking water purification depends on correct pH for its operation.

2. In sugar manufacture, improper pH can result in formation of unwanted acids and very little sugar.

3. In sewage treatment, pH must be adjusted for proper operation of disposal plants. This is, of course, another reason why polluting sewers with high acid or alkaline material spills is undesirable.

4. Milk turns sour at a pH of 6.00. Thus good milk requires good pH control.

5. In old-fashioned jelly making, the pH must be below 4.0. Otherwise, the jelly will not jell.

6. The brightness of chrome coating on our auto bumpers is directly related to the pH of the plating solution.

To sum up, almost every manufacturing process that involves even the simplest chemical reaction is sensitive to pH and will usually produce best results at some optimum pH value. One of the key factors in keeping consistent, uniform products is the ability to measure and maintain pH at the proper level.

WHAT IS pH?

pH is a number that exactly describes the degree of acidity or basicity of a solution. We can make a good analogy with the measurement of temperature. Here we have the terms "cold" and "hot" and we immediately realize that these are very general terms which cannot be used with any degree of accuracy. Accordingly, the temperature scale was developed and now a temperature reading of, say 50°C, means the same to everyone and is scientifically accurate.

In the same way, the pH scale was developed. Centuries ago, man discovered that certain materials possessed properties which he called acid, while others possessed other properties which he called bases. Between these two was a neutral area in which the material showed neither acid or base properties and he termed this a neutral.

Now just as in hot and cold, the words acid and base do not give us a scientific value that we can use. We needed a scale such that we all would be in exact agreement when we discussed the degree of acidity or basicity.

Some time ago a fellow named Sorensen developed such a scale and at the same time came up with the symbol pH.

Before we study the scale, let's take a moment to find out what makes one material an acid while another is a base.

1. An acid must have ionized (or free) hydrogen ions, H^+.

2. A base must have ionised (or free) hydroxyl ions OH^-.

3. The pH is directly related to the ratio of H^+ to OH^-. If the H^+ is greater than OH^- the material is acid. If the OH^- is greater than the H^+, the material is a base. If equal amounts are present, the material is a neutral salt.

Back to the development of the scale. A molar solution of hydrochloric acid is about a 3.6% solution of the acid. Let's assign this solution a pH of 0.

A molar solution of sodium hydroxide (lye) is about a 4.0% solution of the base. Let's assign this solution a pH of 14.

If we now dilute the acid by adding one milliliter of acid to nine milliliters of pure water we will have a 1/10 molar solution. Let's assign this solution a pH of 1. In the same way, let's dilute the molar solution of sodium hydroxide by adding 1 milliliter to 9 milliliters of pure water. We'll assign this resultant solution a pH of 13.

Notice that with the acid, our 1/10th dilution increased the pH from 0 to 1, while the same dilution of the base reduced the pH from 14 to 13. Now here's the significant point - in both cases we were going toward 7. As we'll see shortly, a pH of 7 is the exact middle of the scale at which we have neither acid nor base, but neutral.

Continue to dilute both the acid and base by 1/10th and each time increase the number in the case of the acid and decrease the number in the case of the base.

The results look like this

Acid	pH	Base	pH
1.0 molar	0	1.0 molar	14
0.1 molar	1	0.1 molar	13
0.01 molar	2	0.01 molar	12
0.001 molar	3	0.001 molar	11
0.0001 molar	4	0.0001 molar	10
0.00001 molar	5	0.00001 molar	9
0.000001 molar	6	0.000001 molar	8
0.0000001 molar	7	0.0000001 molar	7

Notice an interesting fact on the acid column - the number of decimal places exactly equals the pH! Therefore a change of 1/10th or 10 times in acid concentration will make a change of 1 pH unit either up or down. The same holds true for bases. A change of either 1/10th or 10 times will change the pH by 1 either up or down.

The following is really not plain language and can be skipped without too great a loss.

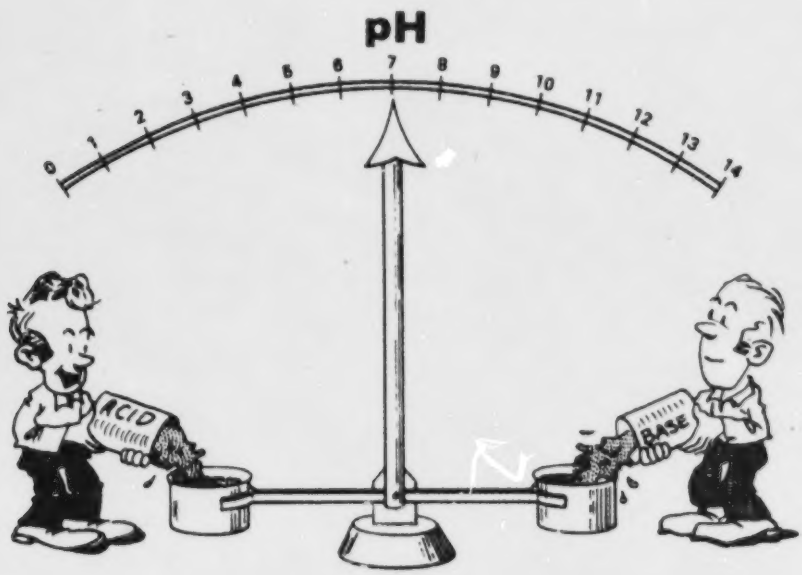
> pH is really a number that is the negative logarithm of the molar concentration of H^+ (hydrogen ions).

Another interesting fact from the chart: if we mix equal volumes of pH 3 (0.001 HCl) and pH 11 (0.001 NaOH), the resultant solution will be a pH of 7. The same applies to 0 and 14, 1 and 13, and so on. Equal amounts of H^+ and OH^- neutralize and result in a pH of 7.

A logical question at this point is "Do all acids and bases act the same?" Unfortunately they do not. The major difference comes in the amount of free H^+ or OH^- that is present in solution. For example, when you dissolve hydrochloric acid in water, all of the hydrogen ions H^+ are free in solution. The same is true of the sodium hydroxide and the hydroxyl ions OH^-. However if you dissolve acetic acid in water, all of the hydrogen ions H^+ are not free (only about 1.3% of the total H^+) and the pH is considerably higher than what you would expect for a molar solution of the acid. Thus, acetic acid (vinegar) is called a weak acid. A good example of a weak base is ammonium hydroxide (household ammonia).

The subject of ionization and dissociation will not be covered here. Just bear in mind that not all acids or bases are completely ionized.

Refer to the scale below to picture just how pH relates to acid and base. Adding acid on the left tips the scale pointer to the left and the number gets smaller (more acidic). Adding base on the right tips the scale pointer to the right and the number gets larger (more basic).



HOW DO WE MEASURE pH?

Although there are paper and dye indicators that change at different pH values, we shall be concerned only with pH meters since we are interested in a precise number that represents the true pH of our solution.

First, there is a pH probe (which we'll discuss shortly) which produces a voltage that can be directly related to the pH of the solution in which we place the probe. Secondly, there is an electronic circuit within the pH meter cabinet that receives the voltage from the probe and then presents it to the meter scale. This voltage developed at the probe will cause the meter pointer to move. The value of the number at which the pointer stops is the pH of the solution.

Let's say we had three separate solutions. No. 1 contains 0.001 molar hydrochloric acid. No. 2 contains pure water and No. 3 contains 0.0001 molar sodium hydroxide.

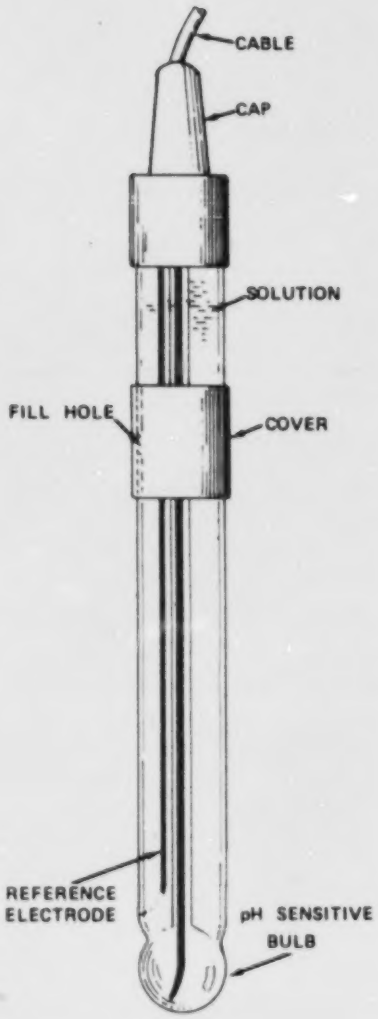
No. 1	No. 2	No. 3
____	____	____

Fill in the blanks with the number that you would expect the pH meter to read as you move the pointer from solution to solution. (If you wrote in No. 1 pH 3, No. 2 pH 7 and No. 3 pH 10, you get 100.)

there are ten small divisions between 7 and 6. Each small division is equal to 0.1 pH units. Thus if the meter pointer came to rest at the fourth small division to the right of the number 6, the pH would be 6.4. If the pointer came to rest between the small divisions, one can estimate and write the value as 6.45.

The shiny strip just below the scale is called mirror-backing. Its purpose is to allow you to look at the pointer and if you see a reflection of the pointer in the mirror you move your head slightly until you cannot see the reflection. This means that you are looking directly at the pointer and therefore the value you read is correct. You can readily see that if two people read the same meter but from different angles, they would report different values. The mirror backed scale helps us all to look at the same angle.

The probe can be thought of as a battery whose voltage changes as the pH of the solution in which it is inserted changes. It consists of two parts (in fact many pH measurements are made with two separate probes), first the hydrogen sensitive glass bulb and second the reference electrode. The special glass of the bulb has the ability to pass H^+. This ability then allows the H^+ inside the bulb to compare themselves with those outside the bulb and to develop a voltage that is related to this difference. This bulb then is a half-cell and will need a companion reference to function.



On the drawing notice that just above the bulb is a reference electrode frit. This is actually a small opening in the glass through which the inside filler solution can very slowly leak out. Now the relationship between the reference electrode and the solution also produces a voltage and this is the other half cell. Together the pH sensitive bulb and the reference electrode constitute the complete probe.

The value of voltage produced by the probe is fortunately a linear function of the pH. For example, at pH 7.00, the probe produces zero volts while at pH 6.00 it produces +0.06 or +60 millivolts. Notice the plus polarity mark; if the voltage were of minus polarity, the meter pointer would go to the right to a pH reading of 8.00.

Generally, a probe will produce about 60 millivolts for each change of 1 pH unit. Thus, a probe voltage of +300 millivolts would cause the meter to read pH 2.00 (+300 ÷ 60 = 5 units, 7 - 2 = 2).

Since the pH meter and probe are both electronic-type devices, you might like to have some standard pH solution that you can measure and be sure that everything is calibrated correctly. These solutions are available and they are called standard buffers. You'll soon find that a buffer is a vital part of all pH measurements.

A buffer is a solution of a particular pH that has the ability to resist change in pH. (By the way, buffers in our blood system are what keeps us alive and healthy.)

Here's an experiment to demonstrate the ability of buffers to resist change. Take two glasses and in one place distilled water. In the second, place a buffer near pH 7.00. Next measure and record the pH at the start. They should both be near 7.00. Now, add one drop of concentrated hydrochloric acid to each glass. Stir, and again record the pH. Do this for several drops with a measurement between each drop. You should find the distilled water drop in pH with each drop. The buffer, on the other hand, should resist change until you exceed its buffering capability.

We won't go into why buffers act this way. Suffice to say it has to do with a phenomenom called common-ion effect. Look it up in your chemistry text.

Temperature is also a very important factor in pH measurements and here's why. We said earlier that the voltage output of a probe was about 60 millivolts per pH unit. However we didn't confuse you by telling you that this is true only at 25°C (room temperature). If you reduce the temperature to 0°C, the probe will provide only about 54 millivolts. And if you increase the temperature to 100°C the probe will provide about 70 millivolts per pH unit.

You can easily see that you must have some way of correcting for this, or make all of your measurements at 25°C.

Let's re-state this situation as a problem and see if we can get a clear understanding of what's happening.

Problem: How to make a pH meter read the correct value of a buffer or sample solution at all temperatures.

Probe output for each pH unit

0°C	54 millivolts
25°C	60 millivolts
50°C	64 millivolts
75°C	68 millivolts
100°C	70 millivolts

In looking at this table we realize that our pH meter must be able to move one pH unit with 54 millivolts input or 70 millivolts or any value in between. Most meters can do this.

Solution: Let us put a sensitive attenuator in the meter and adjust it first to work with 54 millivolts to move 1 pH unit. We'll have a knob on this attenuator and mark the point at which 54 millivolts equalled 1 pH unit. Next, let's move the attenuator to a position where it requires 70 millivolts to move the pointer 1 pH unit. (By the way, we can apply these voltages from a voltage source, and do not require a probe.) In the same way we can set 60 millivolts and so forth. When we are finished we'll have a knob control in which we can set the proper sensitivity of the meter to correspond to the temperature of the sample solution.

Finally, since we are really concerned only with pH (and not millivolts), let's erase the 54 millivolts and write instead 0°C. For the 60 millivolts write 25°C and so forth around the circle.

At this point let's review a little and then we'll make a bona fide pH measurement.

First we discussed the meter and its mirror-backed scale. Next we found that probes are really two-piece affairs (reference and pH sensitive bulb) that produce millivolt outputs and vary with pH. Then the important buffers were described and finally we found that temperature played a vital role in accurate measurements.

To pass the course, we must successfully use this information and produce an accurate pH measurement. Assume for the moment that someone has just handed us a bottle containing a watery solution and asked "What is the pH of this?" Here's how to proceed.

1. Be sure your pH meter has been calibrated and is operating correctly as described in your instruction manual.

2. Turn on the pH meter and allow a few minutes warmup.

3. Set the temperature dial to the temperature of the sample (we will assume that the sample and buffers are at room temperature).

4. Place the pH probe in a 7.00 buffer and position the pointer with the Set knob for a reading of 7.00.

5. Remove the probe, rinse, wipe, and then immerse it in the unknown.

6. Note the reading. If it is near 7.00, record the exact value and the measurement is complete.

7. If it is below 6.00 or above 8.00, then select a buffer that is closest to the unknown. Place the probe in this buffer after a rinse and wipe. Use the Set control to make the meter read exactly the value of the buffer.

8. Remove the probe, rinse, wipe and place in the unknown. Note the reading. The accuracy of this reading will depend primarily on the accuracy of the standard buffer. The closer the buffer value to the unknown, the more accurate the reading.

NOTE: If the unknown in this example had read a value above pH 12.00, you should substitute a special probe that is designed for pH measurement in highly alkaline solution. Most general purpose probes begin to lose accuracy above pH 12.00 due to sodium ion.

Before we end this section on pH measurements, let's discuss another problem and find a solution.

Problem: You are required to measure a series of solutions that may differ by only 0.1 pH units.

Discussion: The meter we described had 10 small marks between each pH unit and each of these marks was 0.1 pH units. In the problem above, it would be very difficult to see the small differences on that meter scale.

Solution: We expand the scale ten times. Thus we use an expanded scale meter and each pH number is now equal to 0.1 pH unit and each small mark equals 0.01 pH unit. Now all we need is a buffer in the vicinity of our unknown and we can easily and accurately make the required measurements.

Of course, we could also have used a digital readout pH meter and read the results directly.

RESIDUE ON EVAPORATION
(Total and Volatile)

PRINCIPLE:

The liquid portion of a sample is evaporated by means of a steam bath or an infra-red lamp. The solid material which represents both the suspended and the dissolved matter is then dried and weighed.

Large floating particles or non-homogeneous particles should be excluded from the sample.

The presence of oil and grease makes it difficult to get a representative sample. They also complicate the drying process.

SAMPLE:

A sample of 100 ml is usually adequate.

EQUIPMENT:

1. Evaporating dish
2. Steam bath or infra-red lamp
3. Drying Oven
4. Desiccator
5. Analytical balance
6. Muffle furnace

PROCEDURE: (For total residue on evaporation)

1. Evaporate 100.0 ml of sample in a tared evaporating dish using a steam bath or an infra-red lamp.
2. Dry to constant weight at 103°C for an hour.
3. Cool in desiccator, and weigh.

PROCEDURE: (For volatile residue on evaporation)

1. After total residue on evaporation has been determined, ignite evaporating dish in a muffle furnace for 15 minutes at 550°C.

Note: When used for volatile residue on evaporation, the evaporating dish must be initially tared after ignition at 550°C for 15 minutes.

CALCULATIONS:

A = Tared weight of evaporating dish

B = Weight of dish and dry residue

C = Weight of dish and residue after ignition in muffle furnace

$$\text{mg/l total residue} = \frac{(B - A) \times 1000}{\text{ml sample}}$$

$$\text{mg/l volatile residue} = \frac{(B - C) \times 1000}{\text{ml sample}}$$

REPORTING:

Two values may be obtained by this method. Report as determined:

mg/l total residue
mg/l volatile residue

SIGNIFICANCE:

This test is most useful in measuring the strength of stong, highly soluble organic wastes. Total residue may be difficult to interpret. Volatile residue of strong wastes may give a good measure of the pollution potential.

REFERENCES:

Standard Methods for the Examination of Water and Wastewater, 13th Edition, 1971, p 536.

SUSPENDED MATTER
(For activated sludge mixed liquor)

PRINCIPLE:

The suspended matter in aeration tank mixed liquors is determined by filtration, drying and weighing. Various methods of filtration such as the aluminum dish in the Buchner funnel, large diameter filter paper in the Buchner funnel, membrane filter holder, Hirsch fritted glass funnel and Gooch crucibles are used.

SAMPLE:

200 milliliters of activated sludge collected at outlet of aeration tank.

APPARATUS:

1. Aluminum dish, with a perforated bottom similar to a Buchner funnel, inside diameter 92 mm, height 25 mm.
2. Filter paper, 90 mm diameter, E & D #615, Whatman #1, or equal.
3. Sponge rubber ring, 93 mm outside diameter, 75 mm inside diameter, thickness about 3 mm.
4. Buchner funnel, #2A, inside diameter at bottom 93 mm.
5. Filter flask, with side tube, 1000 ml size.

PROCEDURE:

Note: Alternatively, one may use a larger diameter filter paper so that the paper extends up the wall of the funnel 1 to 2 cm. This eliminates the need for the aluminum dish.

1. Dry the dish and filter paper in an oven.
2. Cool in a desiccator and weigh.
3. Wet the filter paper in the dish and place dish on the rubber ring in the Buchner funnel.
4. Place Buchner funnel on suction flask and apply vacuum to flask.
5. Add a measured volume of 20 to 100 ml sludge (which should yeild 0.2 to 0.4 g dry solids) to the filter paper in the dish and extract the water.

6. Remove dish with filter paper containing solids and dry in oven at 103° to 105°C for 30 minutes.

7. Cool in the desiccator and weigh.

CALCULATION:

$$\text{mg/l suspended matter (mixed liquor)} = \frac{(\text{wt. of dish \& dry matter} - \text{wt. of dish}) \times 1000}{\text{ml of sample filtered}}$$

SIGNIFICANCE:

This test is used to measure the amount of suspended matter in the aeration tank mixed liquor. The results in mg/l are used in the calculation of SDI and SVI.

REFERENCES:

Standard Methods for the Examination of Water and Wastewater, (12th Edition), 1965; p. 541.

Standard Methods for the Examination of Water and Wastewater, (13th Edition), 1971; pp.537-38 & 560.

The Operation of a "Chicago" Activated Sludge Sewage Treatment Plant, Instruction Booklet 1165-2.

RESIDUE, SUSPENDED
(Total and Volatile)

PRINCIPLE:

Suspended matter is determined by filtration of a sample through a previously tared glass fiber mat and Gooch crucible. The crucible and solids are then dried and weighed, ignited and reweighed for total and volatile solids respectively.

SAMPLE:

A sample of 100 to 1000 ml is required, depending on the concentration of suspended material.

EQUIPMENT & SUPPLIES:

1. Glass Fiber Filter Discs, Reeve Angel 934AH, (312 cm. fits a bitumen Gooch)
2. Filter holder
3. Gooch Crucible (Size of crucible related to size of filter discs)
4. Suction flask, 500 ml
5. Drying oven 103° - 105°C.
6. Desiccator
7. Analytical Balance, 200 g capacity, capable of weighing to 0.1 mg
8. Measuring devices (graduates, pipets)
9. Forceps
10. Vacuum source
11. Muffle furnace

PROCEDURE:

For total Suspended Solids

A. Preparation of tared crucibles.

1. Place fiber disc wrinkled side up in clean gooch crucible which is permanently marked for identification.

2. Place crucible in crucible holder on vacuum flask with vacuum on.

3. Wet filter disc with distilled water.

4. Rinse with 200-300 ml of distilled water.

5. Place crucible in drying oven for 1 hr. at 103° - 105°C.

   Note: If crucible is to be used for volatile solids, it must be ignited at 550°C for 15 minutes.

6. Cool crucible in desiccator and weigh to nearest one-tenth of a milligram.

7. Replace in desiccator until ready for use.

B. Sample analysis for total Suspended Solids.

1. Place tared crucible in crucible holder on vacuum flask.

2. Dampen mat with distilled water and draw rilter disc with vacuum.

3. Measure 100 ml of a thoroughly mixed sample in a graduated cylinder.

4. Filter entire 100 ml of sample. (see notes 1 & 2)

5. Rinse the graduate with two 10 ml portions of distilled water and add each 10 ml portion of rinse water to the filter.

6. Dry crucible at 103° - 105°C for 1 hour.

7. Cool in desiccator and weigh.

Note 1. The entire quantity measured in a graduate must be filtered since solids settle rapidly. Should a sample show evidence of not filtering at a reasonable rate, the procedure should be repeated using an aliquot of the sample.

Note 2. On a clear sample one may want to filter considerably more than 100 ml.

Note 3. If a large amount of solids is trapped on the filter, the crucible may require prolonged drying in order to attain constant weight.

C. Procedure for volatile Suspended Solids

1. After determining the total Suspended Solids on the sample, the crucible is put into a muffle furnace for 20 minutes at 600°C.

2. Cool in desiccator and weigh.

CALCULATIONS:

A = Tared weight of cruible and filter.

B = Total weight of crucible after filtration and drying at 103°C.

C = Total weight of crucible after ignition in muffle furnance.

$$(B-A) \times \frac{1000}{\text{ml of sample}} = \text{mg/l total suspended solids}$$

$$(B-C) \times \frac{1000}{\text{ml of sample}} = \text{mg/l volatile suspended solids.}$$

REPORTING:

Report as mg/liter total suspended solids and mg/liter volatile suspended solids.

SIGNIFICANCE:

On sewage samples, the suspended solids test is quite useful in determining the efficiency of sewage treatment plant settling tanks.

REFERENCES:

Standard Methods For The Examination of Water and Wastewater, (13th Edition), 1971, pp. 537-538.

SETTLEABLE MATTER
(Imhoff Cone Method)

PRINCIPLE:

Settleable matter is determined in a special cone shaped piece of glassware or plastic in which the sewage is allowed to settle for one hour and the volume of the settled material is read from the calibrated tip of the cone.

SAMPLE:

One liter each of raw, primary and final effluents is required.

APPARATUS:

Imhoff cone, support and glass rod.

PROCEDURE:

1. Fill an Imhoff cone to the liter mark with a well mixed sample.
2. Settle for 45 minutes and then very gently stir the sides of the cone with a rod to dislodge suspended material that clings to the tapered sides of the cone.
3. Settle 15 minutes longer and read the volume of settleable matter in ml/liter.

REPORTING:

Report as ml/liter settleable matter.

REFERENCE:

Standard Methods For The Examination of Water and Wastewater, (13th Edition), 1971; p. 539.

SETTLEABILITY
(Graduate method for activated sludge)

PRINCIPLE:

A sample of activated sludge is allowed to settle in a graduated cylinder. For plant control a 30 minute settling period is generally used.

SAMPLE:

One liter of activated sludge.

APPARATUS:

A one-liter graduated cylinder is required.

PROCEDURE:

1. Fill the graduated cylinder to the 1000 ml mark with activated sludge.

2. Read the volume in ml occupied by the sludge at 30 minutes of settling time.

Note: Occasionally it may be helpful to study the settling rate by recording the volume occupied by the sludge at settling times of 5, 10, 20, 30, 45 and 60 minutes.

REPORTING:

Record ml of sludge and length of settling period.

SIGNIFICANCE:

The settleability test is used by plant operators to determine when to increase or decrease the returned sludge rate and when to waste sludge.

REFERENCE:

Standard Methods For The Examination of Water and Wastewater, (13th Edition), 1971; p. 560.

SLUDGE AGE

PRINCIPLE:

Sludge age is defined as the ratio of the total weight of activated sludge in the plant to the weight of suspended solids removed from the daily flow of settled sewage.

Since this is a calculation, certain information is required about the plant and the operation such as volume of aeration tank, daily flow of settled sewage, mg/l suspended matter in the activated sludge and mg/l suspended solids in the primary and final effluents. Procedures in this manual provide methods for obtaining the data on concentration of suspended matter in the activated sludge and the suspended solids on the primary and final effluents.

CALCULATION:

To make the following calculation it is assumed that no sludge blanket exists in the final clarifier:

$$\text{Sludge Age} = \frac{\text{Vol. of aeration tank (mil.gal.)} \times 8.34 \times \text{mg/l susp. matter in aeration tank}}{\text{settled sewage daily flow(mil.gal)} \times 8.34 \times (\text{Prim.eff.SS} - \text{Final Eff.SS in mg/l})}$$

OR

$$= \frac{\text{Total pounds of activated sludge}}{\text{Total pounds SS removed from primary eff. per day}}$$

SIGNIFICANCE:

Generally the older the sludge the higher will be the suspended solids and the lower will be the sludge volume index. Sludge age may be information useful in controlling some plants.

REFERENCE:

Simplified Laboratory Procedures for Wastewater Examination, Water Pollution Control Federation, Publication No. 18, 1971, pp. 34-35.

SLUDGE DENSITY INDEX (SDI)

PRINCIPLE:

The SDI (sludge density index) is a method of measuring the settling quality of activated sludge. It differs from SVI in that the higher the SDI value, the better is the settling quality of the aerated mixed liquor. Similarly, the lower the SDI, the poorer is the settling quality of the mixed liquor. SDI is the concentration in percent solids that the activated sludge will assume after settling 30 minutes.

The results from the suspended solids test and the settleability test, both in the mixed liquor, are used in calculating the SDI. The SDI is also the reciprocal of the sludge volume index (SVI) multiplied by 100.

CALCULATION:

$$SDI = \frac{\text{mg/l suspended solids (mixed liquor)}}{\text{ml settled sludge (mixed liquor)} \times 10}$$

$$SDI = \frac{100}{SVI}$$

SIGNIFICANCE:

Sludge with a SDI of one or more is considered to have good settling characteristics.

REFERENCES:

Standard Methods for the Examination of Water and Wastewater, 13th Edition, 1971, p. 561.

Simplified Laboratory Procedures for Wastewater Examination, Water Pollution Control Federation; Publication No. 18, 1971, p. 34.

SLUDGE SOLIDS
(Total and Volatile)

PRINCIPLE:

Total solids in sludge is a measure of all material present in sludge, both in suspension and in solution. This test is accomplished by evaporating a weighed sample on a steam bath. Unlike total solids in wastewater which is expressed in mg/l, total solids in sludge is expressed in terms of percent by weight of the total amount of solids.

APPARATUS:

1. Evaporating dish.
2. Steam bath.
3. Drying oven.
4. Muffle furnace.
5. Balance capable of weighing to 0.01 gram.

PROCEDURE:

1. Select an evaporating dish that will hold 25-50 grams sludge, clean the dish, place it in a muffle furnace for 15 or 20 minutes. Then air-cool slightly and put the dish in a desiccator for complete cooling before weighing. Weigh dish and record as W_1.
2. Pour a portion of the well-mixed sample (25 to 50 grams) into the dish, then weigh sample and dish together. Record as W_2.
3. Place dish on steam bath and evaporate to dryness. Then put dish in drying oven for 1 hour at 103°C, cool in a desiccator, and weigh. Record the weight as W_3.
4. After weighing the dish and dry solids, compute the percent solids.
5. Place dish from step 4 in muffle furnace at 550°C until the sample is burned completely. The length of time for complete burning depends on the size of the sample.
6. Cool slightly, then put dish in a desiccator for complete cooling before weighing. Weigh the dish and record as W_4. The loss of weight ($W_3 - W_4$) is the volatile solids. The percent volatile solids then may be computed.

$$\text{Percent solids} = \frac{\text{weight of dry solids } (W_3 - W_1)}{\text{weight of wet sludge } (W_2 - W_1)} \times 100$$

$$\text{Percent volatile solids} = \frac{\text{weight of volatile solids } (W_3 - W_4)}{\text{weight of dry solids } (W_3 - W_1)} \times 100$$

SIGNIFICANCE:

The determination of total sludge solids gives a measure of the concentration of the sludge. The volatile sludge solids determined in the raw and digested sludge can give valuable information on the loading of a digester and completeness of digestion.

REFERENCES:

Simplified Laboratory Procedures for Wastewater Examination, Water Pollution Control Federation, Publication No. 18, 1971, pp. 29-30.

Standard Methods for the Examination of Water and Wastewater, 12th Edition, 1965, pp. 534-535.

SLUDGE VOLUME INDEX (SVI)

PRINCIPLE:

The SVI (sludge volume index) of activated sludge is defined as the volume in ml occupied by 1 gram of activated sludge after settling 30 minutes.

The results from the suspended solids test and the settleability test, both on the aerated mixed liquor, are used to calculate the SVI.

CALCULATION:

$$SVI = \frac{\text{ml of settled sludge} \times 1000}{\text{mg/l of suspended matter in mixed liquor}}$$

SIGNIFICANCE:

The lower the SVI, the better is the settling quality of the aerated mixed liquor. High SVI values indicate poor settling qualities. Sludge with a SVI of 100 or less is considered a good settling sludge.

REFERENCES:

Standard Methods for the Examination of Water and Wastewater, 13th Edition, 1971, p. 561.

Simplified Laboratory Procedures for Wastewater Examination, Water Pollution Control Federation, Publication No. 18, 1971, p. 34.

TEMPERATURE

Accurate temperature measurements are necessary to maintain optimum conditions for biological activity such as anaerobic digesters. Temperature readings are necessary for other purposes such as calculating dissolved oxygen saturation values and detection of industrial waters of abnormal temperatures. Many laboratory tests depend upon accurately controlled laboratory test conditions such as the BOD test incubator, bacterial incubator, and drying oven.

Thermometers for field use should be provided with a metal case to minimize breakage. Most thermometers for laboratory use should be the standard laboratory thermometers with a range of -10°C to 110°C. All thermometers should be mercury filled with the centigrade scale subdivided to 1°C. For the fecal coliform incubator, a special thermometer with 0.2°C calibrations is required.

Thermometers are calibrated for either "total-immersion" or "partial-immersion". Total-immersion thermometers must be immersed completely in the medium to be measured to yield the correct temperature. Partial-immersion thermometers differ considerably in that they must be immersed to the depth of the etched circle which appears around the stem below the scale. Thermometers may give inaccurate readings; therefore, all thermometers should be checked periodically against a certified thermometer to determine their accuracy.

Care must be exercised in reading thermometers and temperatures should be recorded to the nearest degree.

Equipment List

Laboratory Tests and Measurements

Quan.	Ch.	
	2.	Acids, organic (colorimetric method)
(1)		A. 6 oz. bottle for sample
(1)		B. Colorimeter or spectrophotometer
(1)		C. Test tube rack for 3/4" test tubes
(8)		D. Test tubes 3/4"
(1)		E. Water bath
(1)		F. Bunsen burner
(1)		G. 2 ml. pipet
(1)		H. 10 ml. pipet
(6)		I. test tube stoppers
	3.	Acids, organic (column chromatographic method)
(1)		A. 6 oz. bottle for sample
(1)		B. Fume hood
(1)		C. Vacuum source
(1)		D. Gooch crucibles, coors No. 3 tall form, or special kontes chromatographic column with extra coarse disc
(1)		E. Crucible holder
(1)		F. Filtering flask - 250 ml.
(1)		G. Buret, 10 ml.
(1)		H. 1 ml. pipet
(1)		I. 5 ml. pipet
(1)		J. Graduates cylinder - 50 ml.
(2)		K. Erlenmeyer flasks - 125 ml.
(1 pkg.)		L. Glass fiber filter paper 2 cm.
(1)		M. Funnel - 65 mm.
(1 pkg.)		N. Filter paper, Whatman #2 - 12.5 cm.
	4.	Acids, volatile (distillation method)
(1)		A. 16 oz. bottle for sample
(1)		B. Centrifuge
(1)		C. 500 ml. round bottom distilling flask
(1)		D. Condenser
(1)		E. Adapter tube
(1)		F. Ring stand support with ring and clamps
(1)		G. Fisher gas burner
(1)		H. Buret, 10 ml.
(1)		I. 250 ml. graduated cylinder
(1)		J. 250 ml. Erlenmeyer flask
	5.	Alkalinity
(1)		A. 10 ml. pipet
(1)		B. 125 ml. Erlenmeyer flask
(1)		C. 10 ml. buret
	6.	Chlorine, Residual
(1)		A. Test tube (25 X 150 mm)
(1)		B. 1000 ml. amber bottle
(1)		C. Chlorine comparator, turbidity compensating

Quan.	Ch.	
	7.	Cyanide (colorimetric method)
(1)		A. 6 oz. bottle for sample
(1)		B. Test tube rack (25 X 150 mm size)
(12)		C. Test tubes (25 X 150 mm)
(6)		D. Test tube stoppers
(2)		E. 1 cm. instrument cell
(1)		F. Pipet - 10 ml., volumetric
(1)		G. Buret, 10 ml.
(1)		H. Volumetric flask, 1000 ml.
	8.	Plant Loading (Incomplete)
	9.	Biochemical oxygen demand (graduate dilution method)
(5)		A. BOD bottles
(1)		B. Siphon
(1)		C. Incubator (D.O. Equipment for BOD
(1)		D. One-liter graduate is listed under Ch. 11)
(1)		E. Plunger-type stirrer
(5)		F. Stoppers for BOD bottles
(1)		G. 5 gal. container for dilution H_2O

Quan.	Ch.	
	10.	Biochemical oxygen demand (simplified non-standard method)
(1)		A. two-quart bottle
(1)		B. 1000 ml.graduated cylinder
(1)		C. Stirring rod
(1)		D. Stopper for 2 quart bottle
(2)		E. BOD bottles
(2)		F. Stoppers for BOD bottles
(1)		G. Incubator
		(Equipment for D.O. test in BOD)
(1)		H. D.O. bottle
(1)		I. Stopper for D.O. bottle
(1)		J. 10 ml. pipet
(1)		K. 250 ml. Erlenmeyer flask
(1)		L. Buret, graduated to 0.1 ml.
(1)		M. D.O. sampler
	11.	Dissolved Oxygen (D.O.)
		(See H - M, Ch. 10)
	12.	Dissolved Oxygen (copper sulfate - sulfamic modification)
(1)		A. D.O. sampler
(1)		B. 10 ml. pipet
(1)		C. 500 ml. Erlenmeyer flask
(1)		D. Buret, graduated to .1 ml.
(3)		E. D.O. bottles
(3)		F. Stoppers for D.O. bottles
(1)		G. Siphon
(1)		H. One quart wide mouth bottle
(1)		I. Stopper for one quart bottle
	13.	Oxygen Demand Index
(1)		A. Electrically heated water bath (kettle of water boiling on an electric hot plate or Bunsen burner is satisfactory)
(1)		B. colorimeter or spectrophotometer with one inch test tube cell or equal
(1)		C. Test tube rack to hold 1 inch test tubes
(1)		D. 10 ml. pipet
(2)		E. 25 X 150 mm test tubes
(1)		F. Measuring spoon
	14.	ph determination
(1)		A. pH probe
(1)		B. pH meter
(1)		C. standard pH solutions (buffers)
(2)		D. 250 ml. beakers
	15.	Residue on evaporation (total and volatile)
(1)		A. Evaporating dish
(1)		B. steam bath or infra-red lamp
(1)		C. drying oven
(1)		D. Desiccator
(1)		E. Analytical balance
(1)		F. Muffle furnace

Quan.	Ch.	
	16.	Mixed liquor, suspended solids (MLSS)
(1)		A. Aluminum dish, with perforated bottom similar to a Buchner funnel, inside diameter 92 mm, height 25 mm.
(1 pkg.)		B. Filter paper, 90 mm diameter, E + D #615, Whatman #1, or equal
(1)		C. Sponge rubber ring, 93 mm outside diameter, 75 mm inside diameter, thickness about 3 mm
(1)		D. Buchner funnel, #2A, inside deameter at bottom 93 mm
(1)		E. Filter flask, with side tube, 1000 ml.
(1)		F. Drying oven
(1)		G. Desiccator
(1)		H. Suction flask
(1)		I. Vacuum pump
	17.	Residue, suspended (Total and volatile)
(1 pkg.)		A. Glass fiber filter discs, reeve angel 934 AH, (312 cm. fits a bitumen Gocch)
(1)		B. Filter holder
(1)		C. Gooch crucible
(1)		D. Suction flask, 500 ml.
(1)		E. Drying oven 103°C - 105°C
(1)		F. Desiccator
(1)		G. Analytical balance, 200g. capacity, capable of weighing to 0.1 mg.
(1)		H. Graduated cylinder, 100 ml.
(1)		I. Measuring pipet, 10 ml.
(1)		J. Forceps
(1)		K. Vacuum pump
(1)		L. Muffle furnace
	18.	Settleable matter (Imhoff Cone Method)
(1)		A. Imhoff cone
(1)		B. Support for Imhoff cone
(1)		C. Glass rod
	19.	Activated Sludge Settleability
(1)		A. One-liter graduated cylinder
	20.	Sludge Age
		A. None (calculation)
	21.	Sludge Density Index
		A. None (calculation)
	22.	Sludge Solids (Total and volatile)
(1)		A. Evaporating dish
(1)		B. Steam bath
(1)		C. Drying oven
(1)		D. Muffle furnace
(1)		E. Balance capable of weighing to 0.01 gram
(1)		F. Desiccator
	23.	Sludge Volume Index (SVI)
		A. None (calculation)

Quan.	Ch.	
	24.	Temperature
(1)		A. Thermometer subdivided to 1°C
(1)		B. Thermometer subdivided to 0.2°C
(1)		C. Total-immersion thermometer
(1)		D. Partial-immersion thermometer

Equipment	Laboratory Test (Chapter Number)																							Quantity	
	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	Max.	Min.
Evaporating Dish														1							1			2	1
Siphon								1			1													2	1
Gooch Crucibles		1														1								2	1
DO Sampler									1	1	1													3	1
Stirring Rod								1(a)	1								1							3	2
1 cm Instrument Cell						2																		2	2
Fume Hood		1																						1	1
Crucible Holder		1																						1	1
Funnel		1(b)													1(c)									2	2
Filter Paper		2(d)													1(e)	1(f)								4	4
Bottles					1(g)				1(h)		1(i)													3	3
Stoppers for Bottles									1(j)		1(k)													2	2
Chlorine Comparator					1																			1	1
5 Gal. Container								1																1	1

a. Plunger Type

b. 65 mm

c. Buchner 93 mm

d. 1 pkg 2 cm; 1 pkg 12.5 cm

e. 1 pkg 90 mm

f. 1 pkg 312 cm discs

g. 1000 ml amber

h. 2 qt.

i. 1 qt.

j. 2 qt.

k. 1 qt.

Equipment	Laboratory Test (Chapter Number)																							Quantity	
	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	Max.	Min.
Aluminum dish, inside diameter 92 mm, ht. 25 mm															1									1	1
Sponge rubber ring 93 mm outside dia. 75 mm inside															1									1	1
Measuring spoon												1												1	1
Beakers, 250 ml													2											2	2
Filter Holder																1								1	1
Forceps																1								1	1
Imhoff Cone																	1							1	1
Support for Imhoff Cone																	1							1	1
Thermometer divided to 1°C																							1	1	1
Thermometer subdivided to 0.2°C																							1	1	1
Total-immersion Thermometer																							1	1	1
Partial-immersion Thermometer																							1	1	1
Sample Bottles	6 oz 1	6 oz 1	16oz 1			6 oz 1																		4	2
Standard pH solutions, buffers													1											1	1

Equipment	Laboratory Test (Chapter Number)																							Quantity	
	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	Max.	Min
Test Tube Rack	1(a)					1(a)						1(b)												3	2
10 ml pipet (measuring)	1			1		1			1	1	1	1				1								8	2
1 ml, 2 ml, 5 ml pipet	1(c)	1(d)																						3	3
Test Tubes 25 mm x 150 mm	8				1	12						2												23	14
Test Tube Stoppers	6					6																		12	6
Buret, 10 ml		1	1	1		1			1	1	1													7	2
Graduated Cylinder		1(e)	1(f)					1(g)	1(h)							1(i)		1(j)						6	5
Erlenmeyer Flasks		1(k)	1(l)	1(m)					1(n)	1(o)	1(p)													7	4
Filtering Flasks		1(q)													1(r)	1(s)								3	3
Volumetric Flasks						1(t)																		1	1
BOD Bottles								5	2															7	5
Stoppers for BOD Bottles								5	2															7	5
DO Bottles									1	1	3													5	3
Stoppers for DO Bottles									1	1	3													5	3

a. 3/4 in.
b. 1 in.
c. 2 ml
d. 1.5 ml
e. 50 ml
f. 250 ml
g. 1 liter
h. 1000 ml
i. 100 ml
j. 1 liter
k. 125 ml
l. 250 ml
m. 125 ml
n. 250 ml
o. 250 ml
p. 500 ml
q. 250 ml
r. 1000 ml
s. 500 ml
t. 1000 ml

Equipment	Laboratory Test (Chapter Number)																								Quantity	
	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24		Max.	Min.
Colorimeter	1											1													2	1
Water Bath	1											1													2	1
Steam Bath														1							1				2	1
Desiccator														1	1	1					1				4	1
Bunsen Burner	1																								1	1
Fisher Gas Burner			1																						1	1
Drying Oven														1	1	1					1				4	1
Centrifuge			1																						1	1
Incubator								1	1																2	1
Vacuum Pump		1													1	1									3	1
Muffle Furnace														1		1					1				3	1
Analytical Balance														1		1					1				3	1
pH Probe													1												1	1
pH Meter													1												1	1
Distillation Apparatus: Condenser, Adapter tube, 500 ml, distilling flask, ring stand with clamps, rings.			1																						1	1